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CELLULOID

ITS MANUFACTURE, APPLICATIONS AND SUBSTITUTES

BY

MASSELON, ROBERTS AND CILLARD

TRANSLATED FROM THE FRENCH BY

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WITH SEVEN PLATES AND OTHER ILLUSTRATIONS

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PREFACE

In viewing the progress that has been made in the manufacture and working of celluloid since its discovery in 1869 by the brothers Hyatt, one cannot fail to be struck by the poverty, to say the least of it, of the literature relating to this substance, the use of which is at the present moment so widespread. Two small volumes only, "Le Celuloïd," by F. R. Boekmann, and "Zelluloïd und seine Verarbeitung" (1908), by Louis Edgar Andes, describe the processes suggested for the manufacture and application of celluloid rather than the processes actually employed in practice. They only convey an exceedingly imperfect notion of the industry.

As a matter of fact, no complete and practical work exists. The modest work which the authors now present will, therefore, not be without utility indeed, the importance which the celluloid industry has attained justifies the work.

It is in a practical spirit, first and foremost, that the book has been conceived. It is no question of confining the task to the re-editing of the descriptions of the numerous laboratory processes and patents—often unused and unusable—which have been put forward for the last forty years. The inadequacy of the two small previous works may be explained by the difficulty of obtaining particulars. Indeed, this is no easy task, and one is constantly met by the opposition of manufacturers guarding the precious secrets of manufacture with a degree of care which is jealous in proportion as the secrets themselves are as often as not "everybody's secret." It therefore becomes necessary to supplement the information by individual knowledge. The authors hope that they have succeeded in producing a work which is complete and, in any case, practical. The processes suggested have been described, but they have particularly laid stress on the descriptions of those which are actually employed in practice; all alike have been conscientiously studied and their relative values discussed.

In order to confer on the work an essentially practical character, the descriptions have been supplemented by numerical data relating to the formulæ of mixtures and of colouring-matters, the duration of the operations, the consumption of raw materials, of steam, of water, the cost of labour and of motive power, and calculations having a direct application to the instalment of workshops and the costs estimated on a given daily output.

The methods of working and the materials have also been studied from a practical point of view, and the authors have been enabled—thanks to the kindness of the builders of machines, to whom they take the opportunity of extending their thanks—copiously to illustrate the volume and to supply the reader with descriptions of the principal types of machines in use.

Notwithstanding the views which may be held by professional men of too exclusive a type, practical considerations never exclude science. Indeed, on the contrary, science is the basis of industry, and every one is agreed at the present day in attributing to the methodical and judicious application of the discoveries of science placed at the service of industry the true cause of the rapid and astonishing success of German industrial progress. It is indubitable that if less empiricism and more science and system had guided the innumerable researches made during the last few years to secure non-inflammability, inventors would not have lost so much time in elaborating so many heterogeneous mixtures of gum, naphthalene, dextrine, colophony, and mineral salts, and would, on the other hand, have bent their efforts in the direction, rather, of research as to the ethers of cellulose.

It will not be surprising, therefore, to find in the present work, side by side with the practical details, purely theoretical investigations, analytical processes, and laboratory researches. Thus, there will be found in the first part most of the opinions, still somewhat controversial, on inflammability and "the theoretical study of nitration baths" by a chemist who, although young, is already justly esteemed, and has a promising career before him—Mr. L. Clément. With regard to the third portion of this work—non-inflammable celluloids and substitutes—this subject, although but subsidiary, is essential in a work which aims at being complete. But, faced with the multiplicity of formulæ, and, above all, with lack of method in their presentation and their general want of success, it was impossible to achieve more than a compilation. Indeed, notwithstanding that the researches have been numerous, the results have been meagre. The want of success has not however disheartened investigators, and new processes arise ceaselessly, so that in spite of the authors' endeavours to make the volume up to date in the latest respect—an endeavour which will explain somewhat the delay which has arisen in regard to its publication, announced long since—they have had to give up the attempt, and to rest content with making monthly summaries in the columns of the publication *Le Caoutchouc et la Gutta-percha*, which have been generously opened to them for that purpose. The reader will find each month in this journal a summary of the latest inventions.

It is to be regretted that the question of the acetates of cellulose, in regard to which it would appear that science seeks to take revenge on empiricism, has not received more attention. The desire was to regard the object of this work as, first and foremost, celluloid, and that substitutes should only take a secondary place. On the other hand, the question is still open to discussion, and it would, perhaps, be premature to draw conclusions. Chemists are not even as yet in agreement as to the constitution of Cross and Bevan's acetate. The authors can hardly dwell much upon this delicate question without going beyond the scope of this work. Possibly it will be necessary some day to indite a work on the acetates, and they hope that others better qualified than themselves for this task will undertake it before long. In conclusion, they hope that they have succeeded in

their object of making the work at once complete and practicable. When first they made their project known encouragement was not lacking, and the numerous subscriptions received prior to publication proved to them that the work was not unnecessary. If it cannot escape criticism—and perfection is in this world unattainable—they hope the reader will extend to them some degree of indulgence, inasmuch as it is the first complete and practical treatise on the celluloid industry, and because the task before them was an arduous one.

M., R. & C.

PARIS.

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PART I. MANUFACTURE

CHAPTER I

COMPOSITION. ORIGIN. PROPERTIES

COMPOSITION AND ORIGIN

Pure celluloid is a substance resulting from a mixture, made under certain conditions, of nitrocellulose and camphor, the latter appearing to play the part of a solvent for the nitrocellulose.

Nitrocellulose is always the basis of celluloid, but the camphor may be replaced by similar substances. Of the latter, however, we may affirm that, whatever be the camphor substitute employed, no product having all the properties and qualities of celluloid manufactured from nitrocellulose and camphor can be obtained.

The invention of celluloid originated in America, where two printers—viz. the brothers Hyatt, of Newark (New Jersey)—discovered it in 1869. (American patent 88634 of April 6, 1869.)

This sensational discovery was not made haphazard, like so many others, and at the time people were unaware that this body, which is so valuable to-day, had a future in store for it. Hyatt Brothers were searching for an unyielding substance suitable for making inking-rollers.

Several investigators, before the brothers Hyatt, had applied themselves to the study of the non-explosive derivatives of nitrocellulose, notably Alexander Parkes, of Burry-Port (Wales), who, many years previous (1855), had produced a substance derived from pyroxylin, to which he gave the name of "Parkesine," and which was intended to replace caoutchouc and gutta-percha. The product was prepared by mixing guncotton and wood naphtha, to which was added castor-oil for rendering it less tough and brittle.

After Parkes, several American chemists took out patents for derivatives of nitrocellulose: W. H. Pierson, of New Orleans (American patent 65267 of April 28, 1867); John MacClelland, of Louisville (American patent of April 28, 1869); Ch. A. Seely of New York (American patent of June 23, 1868); John L. Kendall, of Farborough (patent 86841 of Feb. 9, 1869); Leander R. Streeter, of Chelsea (patent 88228 of March 23, 1869).

About the same period E. Spiers manufactured a very similar product at

Birmingham under the name of Xyloïdine. His Birmingham works were transferred by his successors to London, where they continued for a long time under the name of the British Xyloïd Company.

To Hyatt Brothers, however, belongs indisputably the honour of having established the industrial production of celluloid, and their works at Newark, under the name of the Celluloid Manufacturing Company were the first to manufacture this product on a large scale.

Their process was first employed in France in 1876 at the Stains works, the present property of the Compagnie française du Celluloïd.

This works, which is still among the most important in Europe, was at this period the only one on the Continent, that founded by Magnus at Berlin in 1878 having been destroyed by fire.

Since then numerous works have been established both in Europe and America, the manufacture of this product having undergone great development in America, England, France and Germany. Both the last-named countries some years ago acquired a special reputation for the manufacture of the raw material used in the production of such manufactured articles as combs, beads, instruments, needle-cases, balls, toys, &c.

PROPERTIES OF CELLULOID

Physical properties. Celluloid, obtained by mixing nitrocellulose and camphor, is a non-compressible substance, difficult to twist, and almost untearable. It is slightly brown in colour and is transparent in thin laminæ. The characteristic odour of camphor is evolved, this tending to disappear with time.

The density varies according to the properties of constituents present; 1·35 is taken as the normal density.

One of the chief properties of celluloid is that of softening when heated. Softening takes place from 80° to 90° C., better in boiling water, the rigidity returning on cooling. This property permits the shaping and moulding of objects.

If the heating is accompanied by compression, the celluloid softens and adheres together when moistened.

When heated without compression to a temperature in the neighbourhood of 126° to 130° C., celluloid hardens while losing its transparence; if this temperature be augmented a little, red nitrous vapours are evolved, accompanied by the volatilisation and partial oxidation of the camphor. The nitrocellulose is decomposed and only an ash remains behind.

One of the most serious defects of celluloid is its great inflammability, due to the properties of its constituent elements. When held in a flame it instantly takes fire, evolving thick fumes. If one blows upon celluloid during ignition the flame is extinguished, but the nitrocellulose continues to burn without, however, the production of flame. Nitrocellulose evolves rutilant vapours and, on account of its tardy combustion, the heat generated volatilises the camphor, which is exhaled as a thick white vapour possessing a characteristic odour.

When submitted to concussion or to cold compression, celluloid is non-explosive.

Theoretically the same should apply when warm. Nevertheless, when heated to a temperature of 125° C. accompanied by compression an explosion may take place.

This incidence of compression is fortunately of rare occurrence, being produced by the instantaneous evolution of a large volume of vapour causing a considerable pressure much greater than that imposed by the compression apparatus. Now and then it happens in the stuffing machines; more seldom it occurs in those presses where the pressure is similar to that in the above.

The question of the inflammability and decomposition of celluloid has, however, been strongly contested, owing to the most extraordinary phenomena of spontaneous inflammability related by trustworthy individuals. Combs have taken fire on the head itself; celluloid articles in shops have been kindled in shop-windows. The reports have certainly been much exaggerated in spite of the unquestionable and inherent inflammability of this body.

M. Will, of the Central Research Bureau at Neu-Babelsberg, near Berlin, has devoted himself to the interesting study of the two-fold problem of inflammability and explosibility.

We cannot pass by his investigations in silence, and we shall return to this problem of the inflammability and explosibility of celluloid after dealing with the nature of the product and the mode of manufacture employed, but it would be premature to enter into the detail of the interesting researches of Will, Brunswig, Thieme, A. Voigt, Bronn, and K. Voigt before examining the different manufacturing processes employed in the works.

At this point we shall only summarise, from a communication made by the Central Research Bureau at Neu-Babelsberg, the conclusions arrived at by Will from a large number of experiments carried out by him in collaboration with Doctors Brunswig and Thieme: the experiments will be described later.

Tests have been carried out upon samples of crude and manufactured celluloid taken from the trade, and also on samples made by the ordinary processes at the Central Bureau.

In reality, the great danger of celluloid lies rather in the rapidity with which it continues to burn than in its faculty for spontaneous ignition. M. Will declares that celluloid of good quality is a substance relatively insensible to causes effecting change. It cannot be kindled by shock, friction, electric sparks, or elevation of temperature to 100° C. It may only be ignited by contact with flame, although in this case it burns with great rapidity.

The combustion of plates, sheets or objects ignited by contact with flame, cannot give rise to an explosion, but the celluloid dust produced during the course of working up the latter may by ignition promote deflagration. On the other hand, the gaseous evolution produced during the combustion of celluloid or the deflagration of dust may form with air a detonating mixture.

Will has been careful to speak here of celluloid of good quality. In reality

it is an expression of opinion that the degree of inflammability of celluloid, its explosivity and, in general, its attitude towards external influence, varies considerably with the quality of the celluloid.

This opinion is shared by M. A. Voigt but disputed by K. Voigt. Practical experience, however, appears to support the former, a celluloid of bad quality being probably more susceptible to external influence. In particular, the more neutral the nitrocellulose employed, and the less acid it contains after bleaching and washing, the better the quality of the celluloid. A celluloid proceeding from an insufficiently neutralised nitrocellulose is more susceptible to external agents and exhibits a greater tendency to ignite when heated.

Chemical properties. Celluloid is almost completely insoluble in water; after prolonged immersion, especially in hot water, a very small quantity of the camphor contained in the celluloid is dissolved. Moreover, the water is often tinted owing to incomplete fixation of the colouring-matters.

Celluloid resists the action of most acids in the cold at ordinary concentrations: *e.g.* sulphuric, nitric and hydrochloric. Nevertheless, after prolonged contact and especially with small thicknesses of celluloid or when the latter is divided into small fragments, solution takes place with relative ease. The solubility is increased by heating. The nitrocellulose is dissolved, giving rise to a series of nitrogen compounds.

The camphor is also soluble and on account of the acidic action gives a brown tinge to the mass.

Bases do not attack celluloid in the cold; when boiled with an aqueous solution of caustic soda or potash (at least 150 grammes of NaOH per litre of water) the celluloid is decomposed, causing a great elevation of temperature; the camphor separating from the dissolved celluloid is carried away by the steam evolved and may be recovered.

Glacial acetic acid rapidly dissolves it; if the solution is poured into a sufficiently large volume of water, the nitrocellulose, camphor and other substances are precipitated.

Absolute alcohol in the cold exerts only a slow action on celluloid. Alcohol of 96 per cent. penetrates it more or less rapidly according to the thickness of the mass immersed. The celluloid swells and softens, and it is this property which permits the waste to be readily worked up after suffusion.

If heat is applied solution does not take place, even after a prolonged stay in the alcohol, but decomposition, owing to the solubility of the camphor which is dissolved by the alcohol.

Acetone, either liquid or vapour, rapidly dissolves it. The same applies to sulphuric and acetic ethers, and to mixtures of these with alcohol, acetone, toluene, or amyl acetate. The best commercial solvent for celluloid is camphorated alcohol. This mixture, used in the cold in proportions of 10 parts camphor to 100 parts alcohol, quickly brings about solution.

CHAPTER II

NITROCELLULOSE

GENERAL CHARACTERISTICS.

To nitrocellulose is ascribed the general formula :

$$C_{24}\,H_{40-n}N_n\,O_{20+2n}$$

It results from the action of a mixture of nitric and sulphuric acids on cellulose.

Nitrocellulose is still known under the names of pyroxylin and gun-cotton, which only differ in their nitrogen content.

The maximum degree of nitration theoretically should give 14·14 per cent. of nitrogen, corresponding to cellulose dodecanitrate. In practice, however, cellulose decanitrate may only be produced with difficulty, and quite exceptionally cellulose endecanitrate.

Below are given the different nitrocelluloses which may be prepared, together with their theoretical contents of nitrogen.

It must be well understood that a cellulose corresponding to the theoretical nitrated cellulose cannot be obtained ; even during the best conducted nitrations there are always formed nitrocelluloses made up of a mixture of divers theoretical bodies.

Nitrated Celluloses	Formulæ	Theoretical Nitrogen content
Cellulose dodecanitrate	$C_{24}\,H_{28}\,N_{12}\,O_{44}$	14·14
Cellulose endecanitrate	$C_{24}\,H_{29}\,N_{11}\,O_{42}$	13·47
Cellulose decanitrate	$C_{24}\,H_{30}\,N_{10}\,O_{40}$	12·75
Cellulose nononitrate	$C_{24}\,H_{31}\,N_{9}\,O_{38}$	11·97
Cellulose octonitrate	$C_{24}\,H_{32}\,N_{8}\,O_{36}$	11·11
Cellulose heptanitrate	$C_{24}\,H_{33}\,N_{7}\,O_{34}$	10·18
Cellulose hexanitrate	$C_{24}\,H_{34}\,N_{6}\,O_{32}$	9·13
Cellulose pentanitrate	$C_{24}\,H_{35}\,N_{5}\,O_{30}$	8·32
Cellulose tetranitrate	$C_{24}\,H_{36}\,N_{4}\,O_{28}$	7·65

In every instance nitrocellulose has characteristics analogous to those of the cellulose employed (cotton or paper), generally being a little tougher. It burns with great ease, leaving very little ash ; and evolving nitrous vapours at

temperatures about 172° C. Nitrocellulose may be ignited by shock and may also explode. Sunlight slowly decomposes it.

Nitrocellulose is insoluble in water, methyl alcohol, and ether ; it dissolves in acetone and acetic ester. Its solubility in solvents depends upon the nitrogen content. Certain nitrates of cellulose, containing less than 12 per cent., dissolve readily in ethyl alcohol, while others of superior content are insoluble.

For a long time nitrocellulose was regarded as a nitrated compound, but it was Béchamp, in 1856, who first concluded, from his own investigations, that the nitrocelluloses are the nitric ethers of cellulose, an opinion universally held at the present time. Generally speaking, the sulphuric acid in the sulphonitric mixture is regarded as a dehydrating agent. It appears, however, from the recent researches of A. Saposchnikoff, E. Berl and R. Klaye that a more important part must be assigned to the sulphuric acid during nitration. By comparing the pressure of the nitric acid vapour in the sulphonitric mixture with the nitrogen content of the nitrates formed, the former author concludes that nitration only takes place when the nitric acid enters into the mixture as the hydrate HNO_3 or the hydrate $HNO_3 + H_2O$.

E. Berl and R. Klaye ascribe to sulphuric acid at one and the same time a favourable and a detrimental influence upon nitration (Zeitschrift für das Gesamte Schiess-und Sprengstoffwesen, 1907). The favourable influence lies in the elimination of the water formed during the reactions, which should facilitate the combination of the nitrogen by forming a sulphuric or sulphonitric ester. The unfavourable influence is in the tendency to saponify the nitric ester. It is to this saponification that the authors attribute the incomplete esterification of the cellulose, the nitrogen content of the nitrocellulose being 13·47 per cent., corresponding only to the endecanitrate, while that of the nitrocellulose dodecanitrate is 14·14 per cent. The product formed depends on the speeds of the two reactions, viz., etherification and saponification, speeds which are in opposite directions. This explanation of the incomplete esterification of cellulose appears to them more rational than that according to which this phenomena is attributed to the instability of the nitrated products containing more than 13·5 per cent. of nitrogen, an instability which would break up these products during washing. They have indeed succeeded in establishing the stability of those compounds having the maximum degree of nitration, by nitrating cellulose with nitric anhydride, washing with hot water, and analysing the products immediately after drying, and after an interval of six months. The following are their results :

Analysis made immediately after drying :

0·3002 grammes gave 66·42 c.c. of NO. Therefore 1 gramme would give 221·25 c.c. of NO or 13·86 per cent. of nitrogen.

Analysis made six months afterwards :

0·4374 grammes gave 96·72 c.c. of NO. Therefore 1 gramme corresponds to 221·12 c.c. of NO or 13·84 per cent. of nitrogen.

There has therefore been no loss of nitrogen, and no falling off in the nitrogen

content. Actually the water generated during nitration of the cellulose by N_2O_5 forms nitric acid with the nitric anhydride, and this water produces a partial saponification. There results from these two opposed reactions, a compound containing 13·86 per cent. of nitrogen instead of 14·14 per cent. E. Berl and R. Klaye conclude from the above that the degree of nitration of the cellulose nitrates which are formed depends on the states of the nitric and sulphuric acids in the nitrating mixture; that in addition, the limits between which the concentration of the nitric acid in the mixture varies, together with the favourable and detrimental influence of the sulphuric acid upon nitration, explain the great differences in composition and behaviour of the nitric esters of cellulose which are formed.

To a given composition of the sulphonitric mixture should correspond a definite nitrate of cellulose. For each mixture there should be established a state of equilibrium which is the resultant of the nitrating and saponifying actions of the sulphonitric mixture.

Messrs. Berl and Klaye have studied the nitration of cellulose on the one hand and the denitration of cellulose nitrate on the other.

For this investigation the following nitrosulphuric mixtures were employed:

Mixture I.	H_2O	11·50 per cent.
	H_2SO_4	43·62 ,,
	HNO_3	44·88 ,,
Mixture II.	H_2O	18·00 per cent.
	H_2SO_4	40·40 ,,
	HNO_3	41·60 ,,
Mixture III.	H_2O	19·85 per cent.
	H_2SO_4	39·51 ,,
	HNO_3	40·64 ,,

The nitration experiments have afforded the following results, the temperature and duration of the reaction being taken into account:

Nitration of Cellulose.

Mixture I Reaction Temperature	18°		40°		60°	
Duration in hours	24	92	4	6	1	1½
Percentage Nitrogen content of the product formed	13·46	13·60	13·48	13·53	13·64	13·58

Mixture II Reaction Temperature	18°				40°				60°	
Duration in hours	24	92	168	336	4	6	24	48	1½	3
Percentage Nitrogen content of the product formed	11·81	11·81	11·81	11·97	11·65	11·75	11·83	12·00	11·89	11·99

Mixture III Reaction Temperature	18°		40°	
Duration in hours	24	115	6	24
Percentage Nitrogen content of the product formed	10·61	10·71	10·70	10·70

By the denitration of the nitrates, the authors have arrived at products a little different as regards nitrogen content; the Table below indicates some products obtained by the denitration of nitrations with the same sulphonitric mixtures.

Denitration of Cellulose Nitrates.

Mixture I Reaction Temperature		18°			40°			60°	
Duration in hours		24	92	115	4	6	24	1	1½
Percentage Nitrogen content of the products formed in	1	13·48	13·60	—	13·43	13·58	—	13·42	13·58
	2	13·42	—	13·46	—	13·64	13·43	—	—

The nitrates experimented upon contained: the first N = 12·75; the second, N = 10·93.

Mixture II Reaction Temperature	18°				40°			60°	
Duration in hours	24	92	168	336	4 and 6	24	48	1½	3
Percentage Nitrogen content of the products formed	12·57	12·40	12·37	12·47	12·29	12·27	12·28	12·54	12·38

The nitrogen content of the nitrate tested was N = 13·50.

Mixture III Reaction Temperature		18°		40°	
Duration in hours		24	115	6	24
Percentage Nitrogen content of the products formed	1.	12·17	11·86	11·47	11·53
	2.	11·64	11·50	11·22	11·21

The nitrogen content of the latter nitrates tested was: for the first, N = 13·50 per cent.; for the second, N = 12·75 per cent.

By comparing these Tables with those preceding, it is seen that the products obtained by denitrating the nitrates always contain more nitrogen than the substances obtained by the nitration of cellulose. In addition, temperature and duration of reaction exert considerable influence on the nitrogen content of the product obtained.

Messrs. Berl and Klaye have also noted the degree of viscosity and of solubility in an alcohol-ether mixture, these being intimately related to the preceding data. We cannot enter here into further details.

In every case, from our standpoint, nitrocellulose is of very variable composition, depending upon :

(1) The state of purity and concentration of the nitrosulphuric acid mixture.

(2) The greater or less purity of the cellulose, as well as its state of division.

(3) The time during which the acid is in contact with the cellulose.

(4) The temperature of the bath, etc., etc.

Our first task will be to examine each of these conditions.

THE NITRATION OF CELLULOSE.

THE CHOICE OF ACIDS AND OF CELLULOSE—PERIOD OF CONTACT—TEMPERATURE OF THE BATH.

(1) *ACIDS. Nitric Acids.* The nitric acid used for the production of nitrocellulose should be as pure as possible. Acid containing chlorine must be rejected.

In addition, this acid should contain very little hyponitric acid (at the most 0·20 to 0·25 per cent.). With a greater proportion, the acid will be difficult to use, because, as noted by Wurtz, the sulphonitric mixture is unemployable when it contains more than 3 per cent. of nitrous vapours.

Every advantage will be secured by using concentrated nitric acid, especially if the acid mixture is to be regenerated.

When nitric acid of 48° Baumé is employed its density should not be less than 1·500, and the monohydrate content at least equal to 92 per cent.

But the use of nitric acid of 48° Baumé is inconvenient, especially on account of the difficulty experienced in procuring this acid commercially (the transport being similar to that for explosives). The nitric acid most usually employed is from 40° to 42° Baumé and of density 1·38.

This acid should be quite colourless and contain 61 to 62 per cent. of monohydrate.

In all cases the acids should be homogeneous and not contain organic residues such as straw, rags, twine, etc. During the sealing up of the carboys, sulphur, which is generally used for closing the stoppers on account of its low price, should be carefully prevented from falling into the acid and thereby increasing its content of hyponitric acid, while contaminating the acid at the same time.

Sulphuric Acid. Sulphuric acid only plays a secondary part during nitration. Indeed, its presence is mainly for the purpose of absorbing the water formed during the nitration process. In its absence, the strength of the acid rapidly decreases owing to dilution. We have seen, however, that certain chemists ascribe to it a more complex function.

The sulphuric acid employed for the preparation of the sulphonitric mixture should be concentrated. It should be at least 66° Baumé and contain 95·5 per cent. of sulphuric monohydrate. Also the acid should not contain any lead, iron, etc.

(2) *CELLULOSE.* Whatever may be its form, the cellulose used in the manufacture of celluloid should be as pure as possible (especially free from greasy matters). It may be made from such diverse substances as hemp, flax, paper, cotton, straw, ramie, etc.

We affirm that pure cotton paper and cotton are almost exclusively employed in the celluloid manufacture. It is true that all the celluloses mentioned may be more or less nitrated, yet only the two latter give a nitrocellulose which when dissolved in camphorated alcohol yields a good transparent and almost colourless substance. The nitration of cotton is on the decrease, being superseded by paper made from pure cotton.

The paper, wound on reels more or less thick, is formed almost exclusively from cotton.

In all cases, the paper must be very white, only give a little ash ($\frac{1}{2}$ per cent. at the most), and remain white in the nitration bath. It should be tested for the absence of thick, dark coloured filaments (which are often present in paper made from flax). Without this precaution substances might be obtained giving very bad effects, especially for transparent materials.

In Germany a non-chlorine bleaching process is in use which affords an excellent paper.

Cotton possesses an advantage over paper in requiring a less volume of sulphonitric mixture for nitration. Only 60 to 70 kilogrammes of bath per kilogramme of cotton are necessary.

This advantage, however, is counterbalanced by the greater difficulty encountered than with paper. It has been claimed that cotton dissolves more readily during nitration, which would diminish the yield. Practice, however, appears to indicate the contrary. On the other hand, the use of pure cotton of thickness under 5 to 7 mm. gives a beautiful celluloid which is very transparent; cotton is one of the specialities of the Deutsche Celluloïd Fabrik, which employs it for ambers. The greatest objection of all to cotton is really its high price, which is tending to bring about its entire replacement, since it is only employed for very superior qualities. In every case where cotton is used, it is necessary to take account of the fact that cottons of different brands do not behave alike in a nitration bath.

According to Sanford, the nitration of flax requires a higher temperature than that for cotton (?). He recommends the use of New Zealand flax, and a cotton known by the name of Memphis Star.

Certain firms nitrate the cotton waste proceeding from spinning mills. The employment of this material may hardly be recommended, even for the manufacture of an inferior brand of celluloid.

With regard to paper, it should weigh a constant amount per square metre, and this should lie between 16 and 20 grammes or at the most 30 grammes. Poor results are obtained with heavier paper. Böckmann has mentioned 500 grammes per square metre as being employed in the process at the firm of Stains near Paris.

The paper is dried before use, and may be passed into a drying stove at 24° C. For uniform nitration, 100 kilogrammes of sulphonitric mixture are required

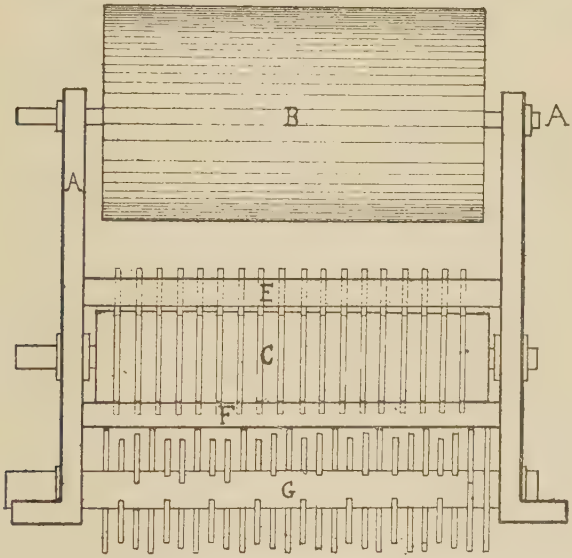


FIG. 1. The Paper-cutting Machine.

per kilogramme of paper. It is well known, however, that this figure may be exceeded; it is even preferable to go to 125 or 130 kilogrammes of acid per kilogramme of paper.

Should the paper be cut up before nitration?

Opinions on this subject are divided.

Sanford says that the Celluloid Manufacturing Company, and also the Xylonite Manufacturing Company, use the paper in sheets from $\frac{5}{400}$ to $\frac{8}{400}$ millimetres thick.

The former cuts them into squares having a side of 25 millimetres; the latter employs long strips 25 millimetres in breadth, which is less advantageous from the yield standpoint.

In many works the paper is unrolled into the sulphonitric bath just as it is, *i.e.* 50 to 60 centimetres in breadth.

Böckmann has described the cutting machine on the previous page. This apparatus is composed of one or more rollers A, capable of turning about an axle resting upon the bearings AA. The paper B is wound upon these rollers. In the Figure only a single roller is represented. The paper is drawn between the two conducting cylinders C, which are furnished with a certain number of annular ribs, between which are inserted the guide wires D. These guides are curved at their extremities and fixed in the upper part of the frame. They descend lower than the under part of the cylinders and are level with the knives G.

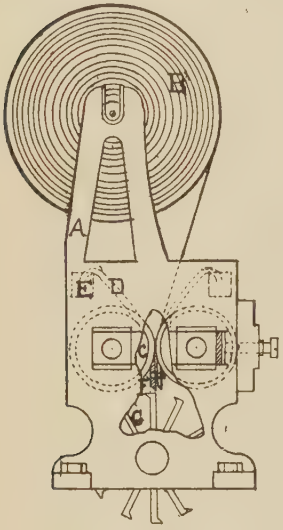


FIG. 2.

These knives are secured upon a movable axle and perform a rotary movement, so that the paper introduced at F is cut by them into small fragments.

(3) *Duration of contact of the acids with the Cellulose.* The time for cellulose to remain in contact with the sulphonitric mixture is extremely variable and differs with each firm.

Some authorities maintain that forty-eight hours are necessary for a complete nitration. Others suppose that the nitration takes place in a few minutes, time being necessary for the nitric acid to penetrate the cellulose fibres. We shall see later when examining the different nitration methods that the intervals vary with each procedure.

We propose, as a normal period, one varying from twenty-seven to thirty-five minutes, this having given us good results after a wide experience. This interval, moreover, varies with the temperature of the nitration bath.

On this question of the duration of immersion of cellulose in the sulphonitric mixture, consult M. Field.[1]

The latter relates to a daily production of 13½ to 16 kilogrammes of pyroxylin for a perion of fourteen consecutive days.

Nitric acid was employed of density slightly less than 1·435. The cotton was used with a sulphonitric mixture made up as follows:

Cotton	1000 grammes
H_2SO_4 (density 1·830)	17·875 kil.
HNO_3 (density 1·435)	9·0625 kil.

which makes 26·9375 kil. of acids per kilogramme of cotton.

Note that the centesimal composition of the sulphonitric mixture is not given. We proceed to calculate this from the given data.

[1] G. Sanford: "Explosifs Nitrés" (Gauthier-Villars).

Sulphuric Acid	17·875 kil. of density 1·830
Nitric Acid	9·0635 kil. of density 1·435

The Tables of Lunge and Naef, and Lunge and Rey, give as the strengths in terms of sulphuric and nitric monohydrates, corresponding to their densities;

Sulphuric acid	92·1 per cent.
Nitric acid	73·42 per cent.

The sulphonitric mixture therefore contains;

$$H_2SO_4 = \frac{92{\cdot}1 \times 17{\cdot}875}{100} = 16{\cdot}462 \text{ kil. monohydrate.}$$

$$HNO_3 = \frac{73{\cdot}42 \times 9{\cdot}0625}{100} = 6{\cdot}607 \text{ kil. monohydrate.}$$

This mixture therefore includes as H_2O:

$$26{\cdot}9375 \text{ kil.} - 23{\cdot}069 = 3{\cdot}868 \text{ kil. } H_2O.$$

The centesimal composition of the acid bath should therefore be approximately;

$$\text{percentage composition} \begin{cases} H_2SO_4 = 61{\cdot}11 \\ HNO_3 = 24{\cdot}52 \\ H_2O = 14{\cdot}37 \end{cases}$$

State of the Weather	Density of the Acids		Duration of the Nitration	Temperature Limits		Gain or Loss in the Yield
	H_2SO_4	HNO_3				
1. Clear	1·838	1·4249	3h. 40m.	57°	62°	+ 31%
2. Clear	1·837	1·4249	1 40	60	62	+ 18
3. Cloudy	1·837	1·4226	1. 15	60	62	+ 7
4. Rainy	1·837	1·420	1	60	63	+ 0
5. Clear	1·8377	1·420	45	58	62	+ 15
6. Rainy	1·8391	1·422	1 15	58	62	− 2
7. Cloudy	1·835	1·4226	15	62	64	− 10
8. Clear	1·835	1·422	35	60	62	+ 5
9. Partially clear	1·824	1·4271	40	50	60	− 3
10. Partially clear	1·83	1·4271	15	58	60	− 10
11. Cloudy	1·832	1·425	40	58	60	+ 8
12. Rainy	1·822	1·425	10	58	60	− 10
13. Partially clear	1·8378	1·4257	50	50	58	+ 20
14. Cloudy	1·837	1·4257	2 44	50	60	+ 16

M. Field remarks that "the examination of the above Table is most instructive. It shows that the yield is susceptible of variations within wide limits. Wet days are unfavourable. This is probably due to the fact that the cotton absorbs moisture from the air, an action which dilutes the acid mixture at the moment of immersion." The author adds: "finally it is important to

remember that nitration at a high temperature gives for each operation different results in every respect."

In the review *Le Caoutchouc et la Gutta-Percha* we have criticised this study in an article from which we give extracts of the more important points.

We affirm that laboratory experiments only afford indications, and that the results differ considerably in the commercial processes.

(1) *Temperature of the bath.* Although high temperatures facilitate nitration, yet in our opinion the temperature of the sulphonitric mixture should never exceed 30 degrees Centigrade. By working at higher temperatures decomposition may take place, which is sometimes dangerous and always prejudicial, giving rise to the formation of nitrous vapours. Further, there is the fear that the nitrocellulose formed may dissolve in the acid mixture, thus causing loss since the nitrocellulose then assumes the condition of an impalpable sediment which cannot be recovered and which renders the clear sulphonitric mixture turbid.

A good average temperature is 25° C. In summer, on account of the heat, this figure tends to be lowered, so that the limits of nitration seldom exceed 25° to 26°.

In a well-conducted nitration, the rise in temperature of the acid bath is almost nil (2° or 3°). The temperature of the sulphonitric mixture is regulated during the preparation either by cooling or heating, as the case may be.

Composition of the sulphonitric mixtures. The composition of these mixtures is of infinite variation. Each firm has recourse to a different recipe. However, the nitrocellulose employed for the celluloid manufacture should approach certain theoretical standards.

The above should vary from cellulose octonitrate to cellulose tetranitrate: in every case as little nitric acid as possible is used for producing a good nitrocellulose.

The following recipes, according to Böckmann, give standard cellulose nitrates.

Cellulose hexanitrate:

(1) { 3 volumes HNO_3 of density 1·517
1 — H_2SO_4 — 1·840

(2) { 3 — H_2SO_4 — 1·800
1 — HNO_3 — 1·500

According to the author, a chemically pure gun-cotton should be obtained by nitrating cotton.

Cellulose tetranitrate:

(1) { 1 volume H_2SO_4 of density 1·840
1 — HNO_3 — 1·380
Duration of nitration: 15 to 30 minutes.
Temperature: 65°.

(2) { 1 volume H_2SO_4 of density 1·840
1 — HNO_3 — 1·400
Duration of nitration : 5 to 10 minutes.
Temperature : 80°.

According to the author, this formula is employed by the firm of Magnes & Co., and it is by a similar process that collodion wool is manufactured at the Fabrik auf Aktien vormals Schering und Co. of Berlin.

Cellulose trinitrate :

4 volumes HNO_3 of density 1·380
5 — H_2SO_4 — 1·840
Duration of nitration : 5 to 10 minutes.
Temperature : 70°.

The following Table contains a *résumé* of some nitration recipes :

Different sulphonitric mixtures used for the production of nitrocellulose for celluloids.[1]

	Composition of the Acid Mixtures	Density of the Acids	Temperature of the Bath	Duration of the Nitration	Observations
I.	7 parts HNO_3 9 „ H_2SO_4	1·43 1·84	50 to 55°	5 to 8 minutes	Nitration of cotton
II.	7 kilogrammes HNO_3 8 „ H_2SO_4	1·42 1·83	Ordinary temperature ?	12 to 14 hours	Nitration of 1 kilog. of cotton
III.	8 parts HNO_3 20 „ H_2SO_4	1·39 1·84	Ordinary temperature ?	12 to 14 hours	Nitration of 1 kilog. of cotton
IV.	20 parts H_2SO_4 9 „ KNO_3	1·84 —	?	Variable	Nitrocellulose dissolved in an alcohol ether mixture
V.	1000 c.c. H_2SO_4 1000 „ HNO_3 272 „ H_2O	1·84 1·47 —	50 to 55°	60 minutes	Nitration of silk paper, yield 140 per cent.
VI.	1000 c.c. H_2SO_4 1000 „ HNO_3 500 „ HNO_3	1·84 1·36 1·47	50 to 55°	60 minutes	Nitration of silk paper, yield 140 per cent.
VII.	7 parts HNO_3 9 „ H_2SO_4	1·43 1·84	45 to 50°	5 to 8 minutes	Nitration of cotton (photographic pellicles).
VIII.[2]	66 parts H_2SO_4 17 „ HNO_3 17 „ H_2O	1·830 1·435 —	30°	20 to 30 minutes	Composition for nitrating from 2·270 kil. to 4·540 kil. of cotton

1 These different compositions are taken from Böckmann's book (Dunod et Pinat, Paris).
2 Recipe given by Sanford.

The following are the results of our own experiments :

The paper nitrated was made from cotton fibre and weighed 18 grammes per square metre.

The sulphuric acid employed was 66° Baumé and of density 1·840.

The nitric acid of 40° Baumé had a density 1·385.

The nitration was made in a plain pot of glazed stoneware.

This cylindrical pot had the following dimensions: height 1500 mm., diameter 650 mm.

NITRATION EXPERIMENTS.

Number of experiment	Centesimal composition of the sulphonitric mixture			Weight of the paper unrolled	Duration of the unrolling	Duration of the nitration	Temperature of the bath		Weight of the dry nitrated paper	Yield per cent.	Nitrogen per cent.
	H_2SO_4	HNO_3	H_2O				Before nitration	After nitration			
				gr.	min.	min.	deg.	deg.	gr.		
1	65·72	15·51	18·77	2500	10	25	24	26	4·022	160·9	10·96
2	67·00	15·17	17·83	2500	11	27	26	28	4·045	161·8	10·93
3	66·53	14·65	18·82	2500	10	27	24	26	3·947	157·9	10·87
4	64·91	14·25	20·84	2500	12	32	23	24	3·907	156·3	10·80
5	71·15	10·79	18·06	2500	10	40	21	24	3·819	152·7	10·49
6	67·89	14·51	17·60	2500	11	26	25	26	4·002	160·1	10·86
7	67·81	13·45	18·74	2500	13	30	24	26	3·872	154·9	10·75
8	68·81	13·55	17·64	2500	11	36	23	26	3·885	155·4	10·78
9	67·83	13·76	18·41	2500	10	34	24	25	3·877	155·1	10·81

The sulphonitric mixture usually employed in celluloid works approaches that given by Sanford in Recipe VIII.

By means of a large number of experiments made in the laboratory of the Stains works, M. Clément (chemical engineer) has investigated the reaction procedure of a nitration bath and the relations connecting together the different bath constants, with the object of establishing a nitration law, from which a rational method of calculation for the bath may be deduced.

The results of these experiments on the mode of action of nitration baths are very interesting, while the conclusions to be drawn from them, as well as the applications which the author has made of his formulæ for deducing practical corrections, afford useful information on the variations of the nitration process. We reproduce at length the work of M. Clément, as set forth in *Le Caoutchouc et la Gutta-Percha* (1909):

THEORETICAL STUDY OF THE NITRATION BATH.

§ 1. *The Theory of Nitration.* Theoretical formulæ for the reactions in a nitration bath may be established in the following way:

(*a*) *Data.* The nitrating bath is composed of: (1) sulphuric acid; (2) nitric acid; (3) water.

Cellulose is introduced into the bath; nitration is produced. What has taken place?

The composition of the bath has evidently changed: nitrogen has disappeared and the water content has been augmented.

The variation in water content during the course of nitration determines the

working of the bath—*i.e.* the way in which the process is carried out. We shall show how this quantity is connected with the degree of nitration of the cellulose.

Let the initial bath contain : x per cent. of H_2SO_4, y „ HNO_3, z „ H_2O } New bath.

Let the final bath contain : x' per cent. of H_2SO_4, y' „ HNO_3, z' „ H_2O } Old bath.

Suppose the nitrocellulose has been nitrated to n per cent. of nitrogen : Degree of *Nitration.*

The variation in water content, viz. $z' - z = a$, is called the *modulus* of the bath.

We have to study the manner in which x, y, z, x', y', z', and n vary. These seven quantities cannot vary at random, so that the functions connecting them are useful to know.

Formulæ will be obtained which shall always satisfy the nitration baths.

Physical conditions (temperature, &c.) give further laws—almost unknown—but it is none the less true that the bath will follow the same rules of composition that we have found.

(*b*) *Theoretical Study of the Nitration.* Two equations may at once be written :

$$x + y + z = 100$$
$$x' + y' + z' = 100$$

Let A be the weight of nitrocellulose formed during nitration, B the weight of the new bath, and B′ the weight of the old bath.

In the following calculations B′ is required, so we proceed at once to find it.

After nitration :

1. The bath has decreased in weight, owing to loss of nitrogen (N fixed as nitrocellulose).

2. The bath has increased in weight, due to the formation of water (combination of the cellulose OH groups with H from the nitric acid).

(As yet there has been no question of the different causes bringing about loss of nitrogen or water. These will be studied in a practical example.)

The following is the equation for nitration :

$$\underset{\text{Cellulose}}{C(OH)_p} + p\underset{\text{Nitric acid}}{(NO_2OH)} = \underset{\text{Nitro-cellulose}}{C(ONO_2)_p} + \underset{\text{Water found}}{pH_2O}$$

The complete equation written by placing on one side all the new bath and on the other all the old bath is :

$$\underbrace{H_2O + H_2SO_4 + HNO_3 + pk(NO_2OH)}_{\text{New bath}} + kC(OH)_p = kC(ONO_2) + \underbrace{pkH_2O + H_2O + HNO_3 + H_2SO_4}_{\text{Old bath}} \qquad (1)$$

k = number of cellulose molecules in contact with the bath;

p = number of replaceable hydroxyls in the cellulose;

$pk\mathrm{NO_2OH}$ = number of acid molecules which disappear in the course of nitration.

It is evident that

$$\text{New bath} - \text{Old bath} = pk(\mathrm{NO_2OH} - \mathrm{H_2O}) = \mathrm{B} - \mathrm{B}'$$

$$\text{Therefore } \mathrm{B} - \mathrm{B}' = 45pk$$

Now let us express the difference of nitric acid content between the two baths:

$$\text{In the new bath there is } \frac{100}{\mathrm{B}y} \text{ of nitric acid,}$$

$$\text{in the old bath } \frac{100}{\mathrm{B}'y'} \qquad (\alpha)$$

By means of the complete nitration equation (1) we see that the difference in nitric acid content is:

$$\mathrm{HNO_3} + pk(\mathrm{NO_2OH}) - \mathrm{HNO_3} = pk(\mathrm{NO_2OH}) = 63pk$$

$$\text{Therefore } \frac{\mathrm{B}y}{100} - \frac{\mathrm{B}'y'}{100} = 63\,pk \qquad (\beta)$$

$$\text{Uniting the equations } \alpha \text{ and } \beta \begin{cases} \mathrm{B} - \mathrm{B}' = 45pk \\ \dfrac{\mathrm{B}y}{100} - \dfrac{\mathrm{B}'y'}{100} = 63pk \end{cases}$$

and eliminating pk from them we have:

$$\mathrm{B}' = \mathrm{B}\left(\frac{5y - 700}{5y' - 700}\right) \qquad \text{(Equation 1)}$$

Equation giving the amount of N taking part in the reaction. The difference in nitrogen content, between the new and old baths, expresses the amount of nitrogen fixed on the cellulose. The quantity of nitrogen contained in a bath is $\frac{14}{63}$ of the nitric acid content.

Therefore:

$$\text{Weight of nitrogen in new bath} = \frac{14}{63}\,\frac{\mathrm{B}y}{100}$$

$$\text{old bath} = \frac{14}{63}\,\frac{\mathrm{B}'y'}{100}$$

$$\text{in the nitrocellulose} = \frac{\mathrm{A}n}{100}$$

$$\text{The equation will be } \frac{14}{63}\left(\frac{\mathrm{B}y}{100} - \frac{\mathrm{B}'y'}{100}\right) = \frac{\mathrm{A}n}{100}$$

Therefore, multiplying throughout by 100 and replacing B′ by its value, we have $\frac{14}{63}\left[By - B\left(\frac{5y - 700}{5y' - 700}\right)y'\right] = An$, which may be written :

$$y - \frac{5y - 700}{5y' - 700}\,y' = \frac{9}{2}\,\frac{An}{B} \qquad \text{(Equation 2)}$$

Equation expressing the amount of water in the bath. The quantity of water contained in the new bath is $\frac{Bz}{100}$ and in the old $\frac{B'z'}{100}$

The increase of water in the bath will therefore be $\frac{1}{100}(B'z' - Bz)$.

Now, for 63 of HNO_3 disappearing, there are 18 of water formed ; for $(By - B'y')$ of HNO_3 disappearing, there are $\frac{18}{63}(By - B'y')$ of water formed, and we shall have :

$$\frac{18}{63}(By - B'y') = B'z' - Bz.$$

Replacing B′ by its value ;

$$\frac{2}{7}\left(By - B\,\frac{5y - 700}{5y' - 700}\,y'\right) = B\,\frac{5y - 700}{5y' - 700}\,z' - Bz.$$

Therefore

$$y - y'\left(\frac{5y - 700}{5y' - 700}\right) = \frac{7}{2}\left(\frac{5y - 700}{5y' - 700}\,z' - z\right) \qquad \text{(Equation 3)}$$

(Independent of the weight of the bath and of the degree of nitration).

To sum up, we have established the equations ;

$$x + y + z = 100 \qquad \text{(A)}$$

$$x' + y' + z' = 100 \qquad \text{(B)}$$

$$y - y'\left(\frac{5y - 700}{5y' - 700}\right) = \frac{9}{2}\,\frac{An}{B} \qquad \text{(C)}$$

$$y - y'\left(\frac{5y - 700}{5y' - 700}\right) = \frac{7}{2}\left(\frac{5y - 700}{5y' - 700}\,z' - z\right) \qquad \text{(D)}$$

Notice that the equations have been established for all the variable quantities of the bath. It is therefore impossible to obtain others for them. Now, for the seven variables, x, y, z, x', y', z', n, we have only four equations. That is to say, three further equations for defining the bath must be furnished by other phenomena, perhaps from physical considerations. We shall endeavour to establish by the elimination of variables a general equation of condition, and it will be seen later how this has been realised.

Calculation of the value $\frac{A}{B}$. First, we shall calculate the value $\frac{A}{B}$ to obtain afterwards a quantity which will serve us in many practical calculations. This value is a constant for a starting bath, since the same amount of cellulose is always introduced into the same weight of acid.

We proceed to calculate $\frac{A}{B}$ for the bath under investigation. It is evident that for another bath it will suffice to change the figures.

Let B = 450 kilogrammes and let 6 kilos. of cellulose be introduced, thus giving A of nitrocellulose. A very simple calculation, which it is unnecessary to reproduce, shows that A = 9·28 k, if we suppose a degree of nitration averaging 11.

$$\text{Therefore } \frac{A}{B} = \frac{9{\cdot}28}{450} = 0{\cdot}020.$$

This constant ratio for a bath will be the *characteristic* of the bath.

Study of the variation in the Degree of Nitration. Many authors have attempted, experimentally, to find a nitration law for celluloses, by bringing about nitration in baths of varying composition. No practical rule, however, has yet been formulated. This is probably due, as we shall see, to the fact that the authors have not taken into account the variation in water content of their bath, *i.e.* their modulus a. Now, the degree of nitration depends upon the above modulus, as we shall demonstrate.

We have just established the two formulæ;

$$y - y'\left(\frac{5y - 700}{5y' - 700}\right) = \frac{9}{2}\frac{An}{B} \qquad (C)$$

$$y - y'\left(\frac{5y - 700}{5y' - 700}\right) = \frac{7}{2}\left(\frac{5y - 700}{5y' - 700}z' - z\right). \qquad (D)$$

From (C) we deduce;

$$\frac{y - \frac{9}{2}\frac{An}{B}}{y'} = \frac{5y - 700}{5y' - 700} \qquad (1)$$

By equating the two last members of (C) and (D) we obtain;

$$\frac{y - \frac{9}{2}\frac{An}{B}}{y'}z' - z = \frac{9}{7}\frac{An}{B}$$

Whence;

$$y' = \frac{\left(y - \frac{9}{2}\frac{An}{B}\right)z'}{z + \frac{9}{7}\frac{An}{B}} \qquad (2)$$

From (1) may also be found the following value for y';

$$y' = \frac{700\left(y - \frac{9}{2}\frac{An}{B}\right)}{700 - \frac{45}{2}\frac{An}{B}} \qquad (3)$$

Equating these two values of y' (2 and 3):

$$\frac{\left(y - \frac{9}{2}\frac{An}{B}\right)z'}{z + \frac{9}{7}\frac{An}{B}} = \frac{700\left(y - \frac{9}{2}\frac{An}{B}\right)}{700 - \frac{45}{2}\frac{An}{B}}$$

Hence:

$$\left(700 - \frac{45}{2}\frac{An}{B}\right)z' = 700\left(z + \frac{9}{7}\frac{An}{B}\right)$$

Replacing z' by $z + a$, the equation becomes:

$$\left(z + a\right)\left(700 - \frac{45}{2}\frac{An}{B}\right) = 700\left(z + \frac{9}{7}\frac{An}{B}\right)$$

$$z = \frac{700a - \frac{45}{2}\frac{An}{B}a - 900\frac{An}{B}}{\frac{45}{2}\frac{An}{B}}$$

Hence:

$$z = \frac{140a - \frac{9}{2}\frac{An}{B}a - 180\frac{An}{B}}{\frac{9}{2}\frac{An}{B}}$$

It is thus evident that the degree of nitration n is a function of z and a.

If $\frac{A}{B}$ be replaced by its value:

$$z = \frac{14a - 0{\cdot}09na - 3{\cdot}6n}{0{\cdot}09a}$$

Curves showing the relationship between z and n have been constructed for different values of a:

$a = 0{\cdot}42$, $a = 0{\cdot}44$, $a = 0{\cdot}40$, &c.

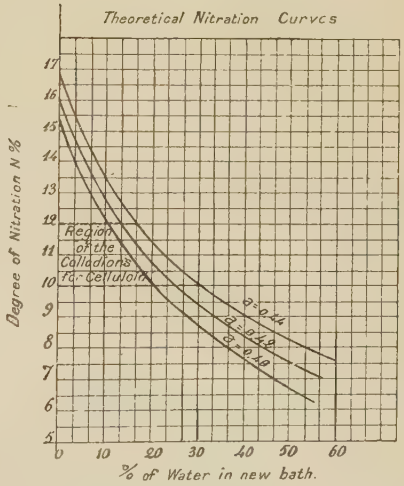


FIG. 3.

These curves are hyperbolas. (Fig. 3.)

Discussion of the formula established. From the theoretical standpoint (and we shall see in the sequel how the practical side of the question is connected

with it) we have to find how z varies in the bath if the degree of nitration n remains constant but a varies. This value of z is connected with a certain composition of the bath.

The following is entirely from a theoretical standpoint:

In a nitrocellulose of constant content n, the amount of water in the bath is a linear function of "a." In other words, if we desire to nitrate always to the

Variations of a as a function of z.

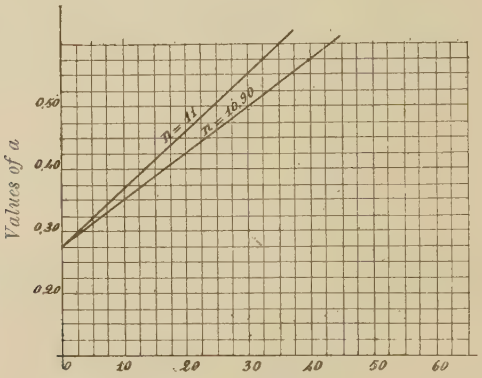


FIG. 4.

same standard, we must take baths having a water content proportional to the increase which they undergo during nitration.

This value of "a" depends also on experimental conditions (temperature, ventilation, &c.).

Should "a" increase, then z must be augmented in order to maintain the nitration bath at its value.

From the practical standpoint, these variations of z as a function of a are much more complex. We shall take an example where a hyperbolic variation has been made.

For the whole series of nitrocelluloses, we may construct the right hand side of z as a function of a:

$$z = \frac{a\,(140 - 0{\cdot}9n) - 3{\cdot}6n}{0{\cdot}05n}$$

According to these functions it is clear that if, for example, in a bath established for nitrating to 11, a variation of the physical conditions is produced such that "a" diminishes, the characteristic point of the nitration will descend and become stationary at another value, 10·9, for example, should the diminution of "a" correspond to this figure.

In the preceding hyperbolas, a variation of n causes the characteristic point to rise or fall upon the different curves, with a bath of given water content; if we desire to increase the degree of nitration, "a" must be increased.

Remarks.

1. The least nitrogen content for a nitrocellulose is 6·7. The curves terminate at this point.

2. Note that all the preceding argument has been on the assumption that a complete nitration has taken place of the whole of the cellulose placed in the bath. There has been no cellulose unattacked, such as usually obtains

NITROCELLULOSE MIXTURES.

In the nitration of cellulose, a mixture of nitrocelluloses will certainly be obtained as a final product. The nitrogen content is the average content. The preceding formulæ established for a standard nitrocellulose may be easily applied to the average nitrocellulose obtained. Indeed, the equation for nitration then becomes :

$$H_2O + H_2SO_4 + HNO_3 + k_1\,C(OH)p_1 + k_2\,C(OH)p_2 + k_3C(OH)p_3 + k_4C(OH)p_4 + k_1p_1(NO_2OH) + k_2p_2\,(NO_2OH) + k_3p_3(NO_2OH) + k_4p_4(NO_2OH) = k_1C(ONO_2)\,p_1 + \ldots\ldots\ k_4C(ONO_2)p_4 + (k_1p_1 + k_2p_2 + k_3p_3 + k_4p_4)\,H_2O + HNO_3 + H_2SO_4 + H_2O.$$

The difference in weight between the new and old baths is :

$$45\ (p_1 + p_2 + p_3 + p_4) \text{ and } \frac{By - B'y'}{100} = 63\ (k_1p_1 + k_2p_2 + k_3p_3 + k_4p_4).$$

The expressions are identical with those obtained at the commencement of this investigation. In fact, it suffices to put :

$$p = \Sigma\, p_1 \text{ and } kp = \Sigma\, k_1p_1$$

Study of the variation of N *as a function of* Y. We have just seen that the degree of nitration depends on z and a. This proportion of water in the bath may be realised in an infinite number of ways by varying the relative proportions of HNO_3 and H_2SO_4. It is true that the formula

$$y - y'\left(\frac{5y - 700}{5y' - 700}\right) = \frac{9}{2}\,\frac{An}{B}$$

gives only a means of varying the degree of nitration by influencing the proportion of nitric acid, but y, which should satisfy this relation, must also satisfy the condition

$$y - y'\left(\frac{5y - 700}{5y' - 700}\right) = \frac{7}{2}\left(\frac{5y - 700}{5y' - 700}\,z' - z\right)$$

It is the combination of these two conditions which has allowed us to establish $z = f(n)$.

In a word, and this is of the greatest importance, the degree of nitration depends solely on the amount of water in the bath and on its behaviour.

Trial determines the relative proportions of HNO_3 and H_2SO_4 in order that the nitrocellulose may neither be too tough nor require too long an interval for its formation.

Theory demands a fixed amount of water for obtaining a nitrocellulose. Practice qualifies the quantity of water by requiring relative proportions of HNO_3 and H_2SO_4 conveniently established by experiment, so as to obtain a nitrocellulose of good physical quality.

A nitrocellulose cannot be obtained independent of the bath.

§ 2. *Practical Corrections.* We have just investigated the ideal bath system, if we may so express it. We have not considered any disturbing cause. In practice it is entirely otherwise, since there are local conditions, such as hydration of the bath, loss of water by ventilation, &c. &c.

For the present we shall study the practical behaviour of the bath, and to account for the disturbances we shall insert *a correction factor* ϕ in the calculations. The disturbances may be regarded as a supplementary modification, positive or negative, of the water in the old bath. ϕ is taken per 100 of water of the old bath.

Hydration, for example (absorption of atmospheric moisture), causes an additional increase to the water of the old bath.

The preceding equations only require simple modification.

The Modified Equations. The amount of correction water is merely added to the whole series of preceding calculations. The general nitration equation becomes:

$$\underset{\text{of the bath}}{H_2O} + H_2SO_4 + HNO_3 + pk\,NO_2OH + k\,C(OH)p + \underset{\text{of the bath}}{H_2O} + \underset{\text{of correction}}{H_2O} =$$

$$= H_2SO_4 + HNO_3 + k\,C(ONO_2)p + kp\,\underset{\text{produced.}}{H_2O}$$

On this occasion there will be:

$$\text{New Bath} - \text{Old Bath} = kp\,(NO_2OH - H_2O) - H_2O \text{ of correction},$$

$$\text{hence: } B - B' = 45\,kp - \frac{B'\phi}{100}$$

$$\text{therefore: } B - B'\left(1 - \frac{\phi}{100}\right) = 45kp. \qquad (1)$$

$$\text{The equation } \frac{By}{100} - \frac{B'y'}{100} = 63\,kp \qquad (2)$$

is always the same, and from (1) and (2) we deduce as before:

$$\frac{B}{B_1} = \frac{5y' + 7(\phi - 100)}{5y - 100} \quad \text{whence: } B' = B\left(\frac{5y - 700}{5y' + 7\phi - 700}\right)$$

The equations being of the same form, it is unnecessary to explain those which relate to the amounts of nitrogen and water, hence we have:

$$y - y'\left(\frac{5y - 700}{5y' + 7\phi - 700}\right) = \frac{9}{2}\frac{An}{B}$$

$$\frac{2}{7}\left(y - y'\frac{5y - 700}{5y' - 700 + 7\phi}\right) = z - z'\frac{5y - 700}{5y' - 700 + 7\phi}$$

The three new operations are therefore:

$$z - z'\left(\frac{5y - 700}{5y' - 700 + 7\phi}\right) = \frac{18}{63}\left[n - y'\frac{y'(5y - 700)}{5y' - 700 + 7\phi}\right] \quad (1)$$

$$y - y'\left(\frac{5y - 700}{5y' - 700 + 7\phi}\right) = \frac{9}{2}\frac{An}{B} \quad (2)$$

$$z - z'\left(\frac{5y - 700}{5y' - 700 + 7\phi}\right) = \frac{9}{7}\frac{An}{B} \quad (3)$$

We shall next deduce the value of z as a function of n, always following the method already adopted.

From (2) we deduce:

$$\frac{5y - 700}{5y' - 700 + 7\phi} = \frac{y - \frac{9}{2}\frac{An}{B}}{y'}$$

From (3) we deduce:

$$z - z'\left(\frac{5y - 700}{5y - 700 + 7\phi}\right) = \frac{9}{7}\frac{An}{B}$$

which may be written:

$$z - z'\left(\frac{y - \frac{9}{2}\frac{An}{B}}{y'}\right) = \frac{9}{7}\frac{An}{B} \qquad y' = z'\frac{\left(y - \frac{9}{2}\frac{An}{B}\right)}{z - \frac{9}{7}\frac{An}{B}} \quad (4)$$

Replacing y' by its value in (4), after having inserted a factor in it, we arrive at:

$$z'\left(700 - \frac{45}{2}\frac{An}{B}\right) = 7(100 - \phi)\left(z - \frac{9}{7}\frac{An}{B}\right) \quad (5)$$

Calculation of ϕ. After a series of four experiments in the works, z, z', and n are replaced in formula (5) by the values found on analysis, ϕ being then deduced.

The results were as follows:

Value of a for the experiment considered	*Value found for* ϕ
$a = 0{\cdot}24$	$\phi = -1{\cdot}74$
$a = 0{\cdot}33$	$\phi = -2{\cdot}21$
$a = 0{\cdot}42$	$\phi = -2{\cdot}68$
$a = 0{\cdot}44$	$\phi = -2{\cdot}83$

If a curve be constructed having as abscissæ the moduli of the bath, and as ordinates the correction factors, it is found to be a straight line (Fig. 5). Whence we have the following law, viz.:

The correction factor is proportional to the modulus of nitration.

This rule is of great convenience.

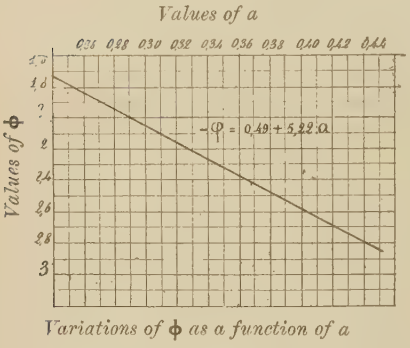


Fig. 5.

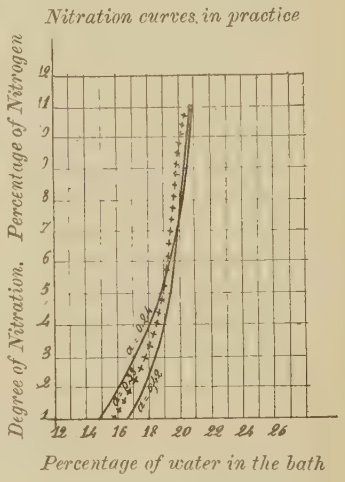

Nitration curves in practice
Degree of Nitration. Percentage of Nitrogen
12 14 16 18 20 22 24 26
Percentage of water in the bath

Fig. 6.

Nitration curves found in practice. It only remains for us to draw the curve for the degree of nitration as a function of the water content when taking into account the correction factor. We have found:

$$z'\left(700 - \frac{45}{2}\frac{An}{B}\right) = 7\,(100 - \phi)\left(z - \frac{9}{7}\frac{An}{B}\right)$$

Replacing z' by $z + a$ we deduce z; it is unnecessary to give the calculation details, we have:

$$z = \frac{700\,a + \frac{An}{B}\left[9\,(100 - \phi) - \frac{45}{2}\,a\right]}{\frac{45}{2}\frac{An}{B} - 7\phi}$$

The curve is always a hyperbola (Fig. 6). We construct it for different values of a.

It is noteworthy that these latest nitration curves are very steep, a small variation of z brings about a much greater variation in the degree of nitration. The variations of z between the limits for celluloid collodions are of the order 1 per cent.

Variations of "z" as a function of "a." On this occasion we have no longer simple proportionality as in the theoretical case.

We have shown ϕ to be of the form: $\phi = p + a\theta$.

Therefore:

$$z = \frac{An}{B} \frac{\left[9\,(100 - (p + \theta a) - \frac{45}{2}\,a)\right] + 700a}{\frac{45}{2}\frac{An}{B} - 7\,(p + \theta a)}$$

which is a hyperbolic function.

The equation connecting ϕ with a is: $-\phi = 0{\cdot}49 + 5{\cdot}22a$, which gives:

$$z = \frac{An}{B} \frac{(904{\cdot}41 + 24{\cdot}48\,a) + 700\,a}{\frac{45}{2}\frac{A}{B}n + 3{\cdot}43 + 36{\cdot}54\,n}$$

It is evident from this example how the bath may be studied.

SUMMARY AND CONCLUSIONS.

As conclusions from this investigation, and as a summary, the following points should be emphasised;

(A) The chemical causes influencing the degree of nitration of cellulose are:

(1) The water content of the bath;

(2) The variation of this content during the nitration process (modulus of nitration).

(B) If conditions be imposed such that the modulus a is constant during each nitration, only the water content has influence on the degree of nitration. The mode of influence, *i.e.* the nitration law, can be found out.

(C) The quantities z, n, a are subject to a relationship between them in a nitration bath.

(D) The relative proportions of H_2SO_4 and HNO_3 are only concerned with practical considerations, such as: the appearance of the nitrocellulose, speed of the reaction, &c. There are no relations between H_2SO and HNO_3 other than practical ones.

(E) The general nitration formula is theoretically:

$$100 - (x + y) = \frac{14a - \frac{9}{2}\frac{An}{B}a - 180\frac{An}{B}}{\frac{9}{2}\frac{An}{B}}$$

The quantities x, y, n, a therefore do not vary haphazard; theoretically they should satisfy the above law, in practice a modified one.

(F) It has been proved that a practical study of the bath may be made by modifying the theoretical formulæ to satisfy special or local influences and disturbances.

Nitration rules may be deduced.

CHAPTER III

COMMERCIAL NITRATION PROCESSES

In this chapter some nitration processes are summarised, certain of which are given by Böckmann in his book on celluloid.

Abel's Process.

Cotton waste is used.

Nitration is carried out in a sulphonitric mixture having the following composition :

1 part H_2SO_4 of density 1·84.
1 part HNO_3 of density 1·48.

Duration of contact : 24 hours.

Dried.—Washed with much water.

Repeated drying and washing.

Pulpation of the nitrocellulose.

The latter is then left two or three days in boiling water.

Dried.

This process is inconvenient in several ways :

(1) The excessive richness of the bath in nitric acid appreciably augments the net cost of the nitrocellulose.

(2) The duration of contact only allows, in practice, of a very limited production.

(3) Washing in boiling water requires an increase in steam production, which everywhere tends naturally to be at a minimum.

Hyatt's Process (worked at New York).—The nitration is conducted in the following apparatus (Fig. 7).

A cylindrical receiver A has at its centre a vertical stirrer, capable of being removed from the nitration pot. This pot is placed on a turning plate B, which, by rotating, can carry it under the crane C. The latter permits the contents of the pot to be poured into an hydro-extractor D. The sulphonitric mixture flows away by the pipe E into an acid tank F.

The tank G contains fresh sulphonitric mixture.

These tanks are hermetically closed, the acids being withdrawn by means of compressed air which arrives through the pipes H H^1.

This nitration system has the inconvenience of requiring many workmen for the nitration of a few kilogrammes of paper.

The large space required in a works by five or six structures of this character to assure an output will be self-evident. Nevertheless, it is by this process, patented in 1878 (American patent 210611), that the Celluloid Manufacturing Company of New York nitrates its cellulose in the Newark works, and

numerous patents have since been taken out for the regeneration of the sulphonitric baths.

The purification of the acids in use has been obtained, according to the American patent 251938 (1882), by the addition of powdered barium sulphate, which carries down an insoluble precipitate.

The regeneration of the same baths whose acids have been purified is brought about by the addition of fresh acid, either nitric or a sulphonitric mixture of convenient proportions (Patent 274335, 1883).

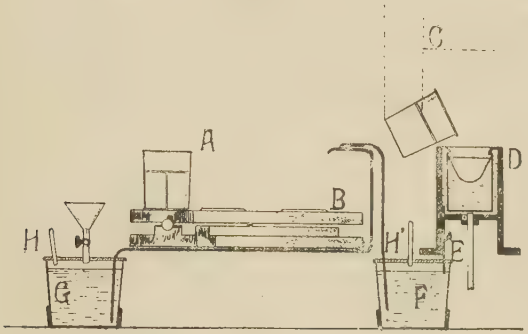


FIG. 7.

The following patents recommend the use of nitrates (Patent 306519, 1884) which are decomposed by sulphuric acid giving an insoluble precipitate and generating nitric acid. In order to compensate the loss of sulphuric acid resulting from the sulphate formation, Patent 386822 (1886) provides for the simultaneous addition of a nitrate and sulphuric acid. The nitrates specified in Patent 343850 (1886) are those of lead, calcium, barium, or strontium, which, by forming an insoluble precipitate, purify and regenerate the bath at one and the same time.

Finally, the same company took out a patent in 1884 for a special apparatus for manipulation and use in acid baths employed more particularly for the manufacture of soluble nitrocellulose (American patent 299388).

Lenk's Process.

This employs cotton.

The above is washed with a boiling solution of caustic potash for two or three minutes.

Hydro-extracted, washed with water, again hydro-extracted, then dried.

The nitration is by means of a mixture of :

3 parts H_2SO_4 of density 1·84.

1 part HNO_3 of density 1·40.

Duration of nitration : a few minutes.

Drained.

Placed two days in stoneware vessels.

Washed with much water. Hydro-extracted.

The nitrocellulose is left for three or six weeks in running water. Again washed with slightly alkaline water, then with ordinary water. Finally hydro-extracted and dried.

This process presents, over the preceding ones, the inconvenience of requiring a very long time for manufacture, which increases the whole cost of production, thus prohibiting its use. It has not received commercial application on this account. The extreme slowness of such a process will readily be comprehended.

(1) It has the shortest nitration period, a few minutes, but the latter is completed by allowing the nitrocellulose to remain two days in earthenware pots.

(2) After a washing and hydro-extraction the nitrated paper is placed in running water, and left for three to six weeks.

(3) Renewed washings.

What can we conclude for the daily production of such a nitration, which ought to furnish 1000 or 1500 kilogrammes of nitrocellulose?

Process employed by La Cie de Celluloid, near Paris. According to Böckmann, this firm employs concentrated nitric acid with a little sulphuric acid added, for nitration.

The paper to be nitrated (linen or cotton paper) should weigh about 500 grammes per square metre.

In this case, it is not paper but cardboard which is nitrated, and we can hardly credit the satisfactory results claimed for it. We are willing to believe that this firm has never nitrated under such conditions. It must be an error on the part of the above author. We have tried to nitrate paper weighing 32 to 35 grammes, which is of less weight than that indicated in the above process, yet nevertheless the attempted nitration was very defective.

The unrolled paper, in contact with the sulphonitric mixture, hardens in the first instance and becomes brittle towards the end of the operation. The paper contracts. At the close of the nitration, and the duration of the latter is sensibly increased by giving the acid time to penetrate thoroughly into the interior of the paper fibres, an unsatisfactory yield was obtained, since much of the nitrocellulose was found dissolved in the acid bath. The latter constitutes a very strong objection to the use of cellulose in the form of cardboard.

The words "with a little sulphuric acid added," point apparently to a very small proportion of this acid, which is a further source of error.

The following description, given by M. Séguin, works inspector at Paris,[1] is certainly more reliable.

The cellulose employed is paper made from pure cotton rags. The paper arrives at the works in rolls of thin sheets and is cut into ribbons about a centimètre in width. These paper ribbons, which contain about 2 per cent. to 3 per cent. water, are placed at least 24 hours in a drying chamber.

[1] "Bulletin de l'Inspection du Travail," 1904, Nos. 3 and 4. Note on the manufacture of celluloid, by M. Séguin, Departmental Works Inspector at Paris.

The strength of the nitric acid employed is 40° to 45° Baumé, that of the sulphuric acid 66° Baumé.

The acids are conveyed from the carboys into an iron receiver by means of compressed air. In this receiver both acids are mixed in the proportion of 100 sulphuric acid to 50 nitric acid. The mixture is next transmitted, always by compressed air, to large closed metallic tanks; the latter supply a basin in which to the new mixture is added some of the acid remaining over from preceding nitrations. By a suitable proportion of the two mixtures the necessary concentration is arrived at for obtaining cellulose octonitrate without having to add water.

The paper proceeding from the drying-room is placed in a prismatic basket of perforated sheet iron, which is put into a truck on rails and brought under a

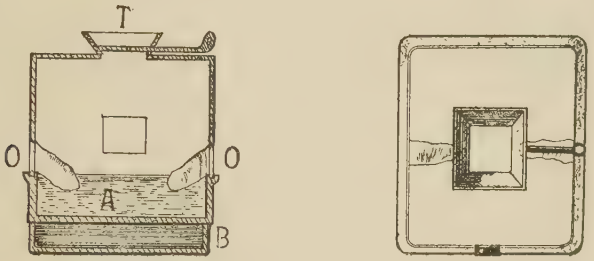


FIG. 8.

tap connected with the basin containing the workshop mixtures. From this tap is run the necessary quantity of the sulphonitric mixture, and the paper then mashed by a long iron fork whose handle is protected by a pommel.

The nitration having been brought about by the mashing, a hand-winch withdraws the basket from the truck. The nitrated paper is drained in a hydro-extractor which expresses the excess of acid, then thrown into a vat lined with lead, containing a large volume of water.

The object of this immersion in water is to prevent further attack by traces of acid remaining after the hydro-extraction.

The acid mixture remaining in the trucks, together with that expressed during the hydro-extraction, is recovered by a pump and conveyed to the mixing room in order to be added to a fresh mixture.

The nitrocellulose thus obtained is afterwards washed in lead-lined vats for some time in water, and then transferred to the bleaching section.

The Process of Tribouillet and L. A. de Bésancèle of Paris. In this process the apparatus used is represented in Fig. 8.

This apparatus is either of glass or enamelled sheet iron, its height is from 15 to 20 centimètres, and the shape, as indicated by Figure 8, is cubical.

The nitration is performed in a tank A, having a double bottom B, into which either water or steam may be introduced so as to cool or heat the bath.

At the top of the tank containing the sulphonitric mixture is a funnel T, into which the material to be nitrated is fed.

Finally, on each side of the tank A are the openings O, O, furnished with rubber sleeves through which the mass may be mashed.

The cellulose (cotton, paper, &c.), dried at 100° C., is ground and nitrated in the above apparatus.

The following sulphonitric mixture is employed :

2 parts HNO_3 of density 1·50.
3 parts H_2SO_4 of density 1·84.

"The nitric acid must contain nitrous fumes."

The precaution must be taken, however, not to employ this bath until the cellulose has been allowed to remain for 10 to 15 minutes in a mixture previously used.

The nitrated product obtained is squeezed by a hand press.

We shall not describe the device employed for washing the crushed nitrocellulose.

This method of nitration not only requires laborious work on the part of the operator, but obviously can only give defective results.

In other nitration processes the formation of powdered nitrocellulose is avoided, since it is very difficult to recover ; in the above process the contrary is the case. Further, the use of nitric acid rich in hyponitric acid is recommended. Good results are impossible under these conditions. Also, from considerations other than those mentioned, this process has not received industrial application.

One may hardly conceive an installation of this apparatus producing 1500 kilogrammes of nitrocellulose per day.

Mowbray's Process at North-Adams. This process presents many differences from those preceding, this consisting of :

1. Hot calendering of unsized paper and direct passage into the acid bath.

2. Pressing the nitrated paper on leaving the bath ; washing of the endless band which has been nitrated and pressed.

3. Drying the band ; moistening this by an appropriate liquid and then winding up.

Below is a description of this apparatus, the scheme represented in Fig. 9 showing a section of the installation.

A shaft, 2, fitted in the frame, 1, carries the paper to be nitrated, 3. In addition, this frame carries six hollow cylinders (4, 5, 6, 7, 8 and 9) capable of receiving steam within.

The paper passes over the outer surface of these heated cylinders, thus tending to lose its moisture.

Also mounted on the shaft 2, which carries the roll to be unwound, is a cylinder 2′, having teeth in its periphery, whose object is to perforate the paper

from place to place. By this means the action of the sulphonitric mixture is rendered more rapid and complete.

After passing between the six drying cylinders, the paper to be nitrated arrives between two rollers, the one a conducting roller, 13, the other serving as a support. The latter is surmounted by a scraping roller.

The paper next falls into the vat 10.

The latter, of truncated form, contains the sulphonitric mixture of known strength destined for the nitration. In this vat is a worm 11 through which

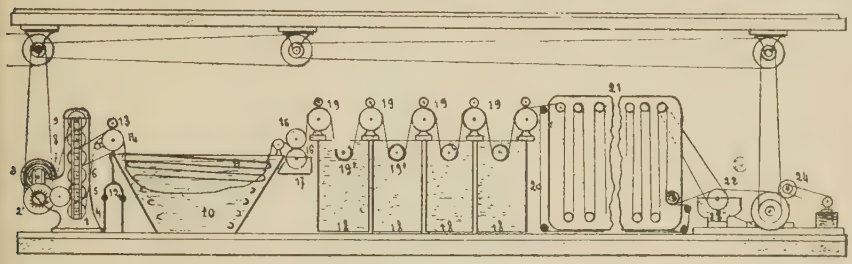


FIG. 9.

water or steam may be passed by means of the pipe system 12, so as to cool or heat the acid mixture.

After emerging from the nitration bath, the paper passes between two press rollers 15 and 16. The acid expressed by these rotary cylinders flows into the receiver 17, placed immediately underneath.

The washing next takes place.

The washers 18, four in number, are tanks in which the paper comes into contact with water. The paper passes in the first place over a roller 19, fixed above the washer. Then it arrives upon a conducting cylinder 19′, situated inside the wash vat.

The paper containing no trace of acid—a statement which we doubt, on account of the small quantity of water which has been in contact with it—is dried.

For this purpose it is fed to an endless belt 20, which carries it into a drying chamber 21, where it passes over hollow, steam-heated cylinders.

No mention, unfortunately, is made of the temperature to which the cylinders are heated, or that of the atmosphere in the drying chamber. In every respect this system should offer good security.

The nitrated paper when dry arrives upon a channelled cylinder 22, placed above a receiver 23, which contains camphorated alcohol, or any other solvent ordinarily employed for suffusion. The cylinder also acts as a conductor, distributing the solvent uniformly on the surface of the nitrocellulose belt.

Finally, the almost formed collodion may either be wound upon a roller 24, or merely passed into a suffusion box.

The value of the process. Böckmann states that this process considerably reduces the cost of production necessitated by the processes usually employed for

the manufacture of nitrocellulose. He adds that this cost is reduced by the important diminution in staff, and that a nitrocellulose is also obtained rapidly and with limited manipulation ready to be transferred into celluloid.

We shall consider the value of this process from a different standpoint.

(1) In our opinion the unwound paper, after its sojourn in the sulphonitric mixture (a period varying from ten to twenty minutes), hardly possesses sufficient strength, the more so as it is perforated, as we have already mentioned, by numerous holes. We are persuaded also that the paper will have been broken many times during nitration. Some manipulations necessary for improving the substances must therefore be tried. This defect may perhaps be remedied within limits, by employing a special mixture. The best method would be to pass the unwound paper, before nitration, into a sulphuric acid bath of known composition which would parchment the paper, thus securing a greater resistance to tensile stress.

(2) The washing appears to us insufficient. If the paper had been fed to the bottom of the wash vats, there would have been less chance for the paper to retain acid. It is, moreover, probable that the last bath contains water made slightly alkaline by ammonia, soda, or an alkaline carbonate.

(3) The system, so described, does away with bleaching. In our opinion a process should be found including bleaching. This drawback is most probably due to the fact that without reducing the nitrocellulose to pulp bleaching would not be very efficacious. On the other hand, the time required by the operation, all the proportions remaining as before, is sensibly greater than the duration of nitration and washing.

(4) The system of drying appears dangerous to us; our opinion has already been given on this matter.

(5) The winding up of the paper, after its passage through the solvent tank, appears to present many chances of being unsuccessful, unless it is carried out after passage through a bath weak in camphor, which is not consonant with the object sought. It is true that we may always remove this section of the apparatus and merely send the nitrated paper to a suffusion box or similar apparatus.

To sum up. This process, which theoretically is an ideal one, does not present great interest from the practical standpoint—at least, with respect to the advantages claimed for it by the inventor.

In addition, to secure the output of an average works, many such installations would be necessary, occupying a considerable space; the difficulties of management and the number of operations would be necessarily augmented, while the nitration system itself does not satisfy the conditions required.

The titles only will be given of the numerous patents taken out by Prof. Mowbray in connection with the process above described.

Patent 350497 (1886) deals with the regeneration of the sulphonitric baths.

Patent 350498 (1886) deals with the substitution of nitration vessels made of Bessemer steel for stoneware pots.

Patents 434287, 434288, 443105 (1890), deal with the process just described.

Prof. Mowbray took out these patents when managing the works of the American Zylonite Co. of New York, works which have long since been closed.

Selwig and Lange's Process. The nitration turbine is used in this process. (Figs. 10 and 11.)

This presents the following particulars:

The cage *d*, having a central axle of truncated section *f*, is mounted by a

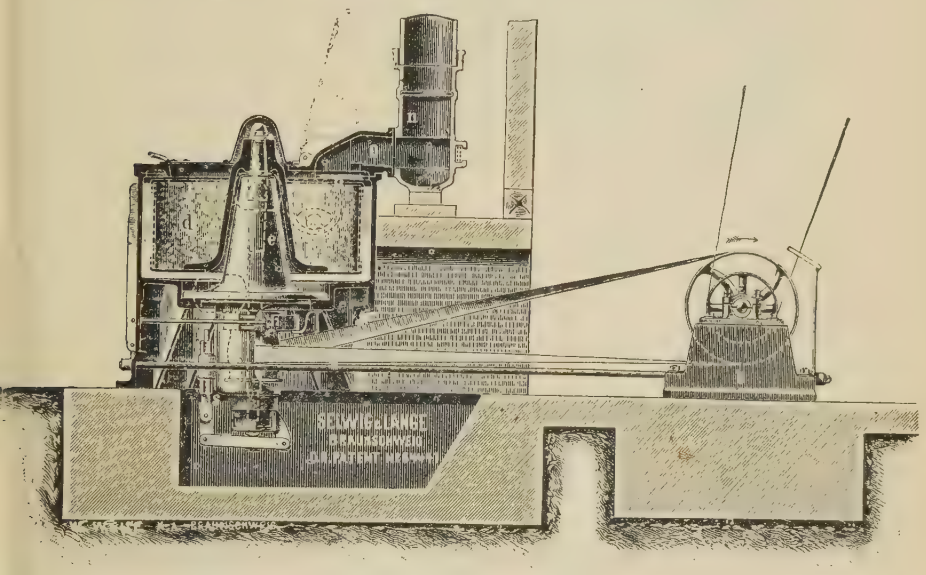


Fig. 10. Elevation.

bearing upon a vertical shaft whose socket just rests on a fixed pivot. This truncated piece is perforated by a large number of holes. Surrounding the cage, which is similarly perforated about its periphery, is an iron cage forming a tank.

A little above the horizontal bed of the case is a second partition *r*, which presents a different profile on each side. On one side the partition almost touches the cylindrical extension of the central truncated axle; on the other it terminates a short distance from the vertical wall of the case.

By this arrangement the interior of the truncated portion may communicate directly with the outer part of the space between the cage and the case, on account of the double bottom. (Fig. 12.)

The cage and the case of the centrifugaliser may receive acid simultaneously.

A tap of ample dimensions *h*, which may be replaced, if desired, by a steel

valve, allows the sulphonitric mixture to be drawn off when the nitration is at an end. A second tap *r*, of more limited dimensions, serves to separate the acid proceeding from the turbine.

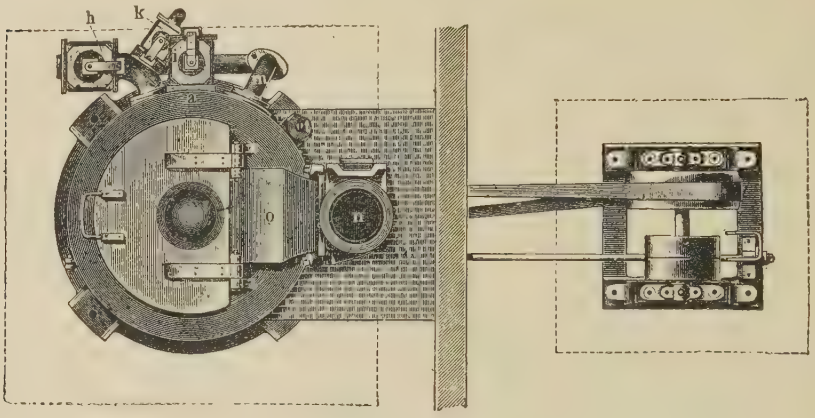


Fig. 11. Plan.

Above the cage, fitted into the cover, is a neck *o*, communicating with an exhaust chimney *n*.

The course which the acid takes during the revolution of the turbine will now be examined.

If the turbine is run at low speed (tweny-four to thirty revolutions per minute), after being previously charged with acid to a given level, the acid is seen, on account of centrifugal force, to take part in the movement. (Fig. 13.)

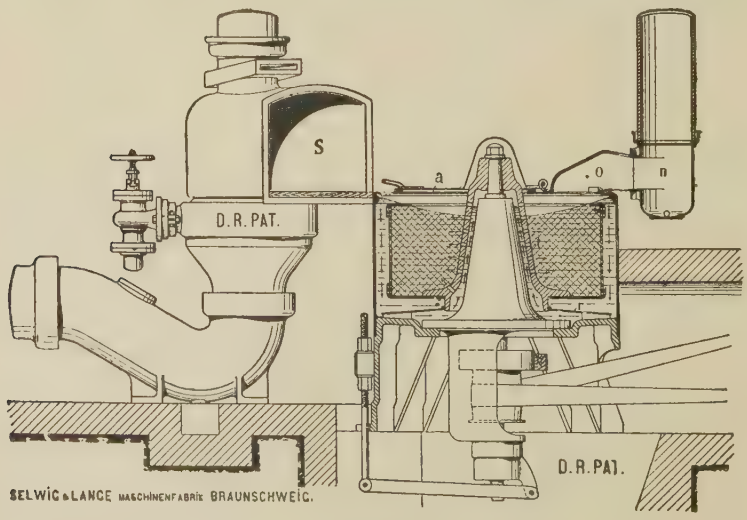


Fig. 12.

At the centre, against the walls of the truncated axle, the level of the sulphonitric mixture falls, while along the case walls of the centrifugaliser it rises.

At this side a greater pressure is produced than exists at the centre of the turbine. An acid current is therefore induced which passes through the holes by which the cone is perforated, since the pressure is also feeble in the hollow space of the conical frustum.

A circulation of acid is set up, penetrating the cellulose to be nitrated, proceeding from the centre of the centrifugaliser to the circumference by passing through the holes in the cage, and returning, after having run under the double bottom, to the hollow space of the conical frustum.

This circulation only ceases when the turbine is no longer in rotation.

The mode of Working the Apparatus. The following are the different working phases of the turbine:

In the first place the intermediate guide pulley is thrown into gear, giving a slow rotation (about 30 revolutions per minute).

The sulphonitric mixture is next introduced and the admission tap closed when the acid is almost level with the brim of the cage—note that the necessary space is allowed for accommodating the cellulose to be nitrated. While the turbine is filling, the paper or cotton which it is proposed to nitrate may be placed in the cage.

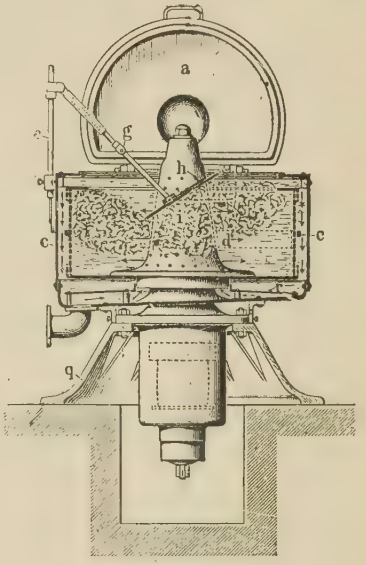


FIG. 13.

When the cellulose is immersed and the turbine steadily rotating, nitration commences and lasts from 25 to 35 minutes.

The nitration being at an end, the acid is drawn off by the tap *h*.

When all the acid has run out, the low speed gear is disengaged, and the high speed pulley thrown into action (1000 to 1100 revolutions).

The nitrocellulose remaining in the pan is hydro-extracted and the expressed acid is drawn off by the tap *k*.

The nitrated paper having been drained is fed into a washing vat or, better, into a poaching machine which will be described later.

One defect of this nitration process lies in the difficulty of steeping the cellulose in the acid bath. To ameliorate this difficulty, the makers deliver a steeping apparatus which obviates the manual labour necessitated by this otherwise inconvenient operation.

This apparatus consists of an aluminium strip *i* known as the "deviator." (Fig. 13.)

The deviator is secured by hinges to an oblique cross piece *h*, which is fixed to the cover of the turbine. It is also fastened to a fixed support *e*, by means of an elastic connection *g*.

In short, the steeping apparatus occupies the space between the truncated axle of the turbine and the walls of the cage.

The following is what takes place during the course of the nitration : while the turbine charged with acid is making about 30 revolutions per minute, the cellulose to be nitrated is placed in the cage in small quantities at a time.

The cellulose strikes the lower face of the deviator, which is almost completely immersed in the sulphonitric mixture ; the cellulose is therefore forced into the acid mixture by passing under the deviator.

The Transporter. With Selwig and Lange's nitration turbine is associated a hydraulic transporter which permits the automatic transference of the nitrocellulose after draining in the centrifugaliser. The transporter, which is placed at the side of the turbine, consists of a stoneware or aluminium hopper whose basal section has a diameter of 25 centimètres.

A little below the upper edge of the hopper a stream of water is allowed to flow delivering 400 to 500 litres per minute.

Above the hopper is a hood into which are drawn the fumes by an exhaust, while below is a pipe having the form of an inverted siphon.

The nitrocellulose, when placed in the funnel, falls into this pipe, comes into contact with the large volume of water flowing through it, and is thereby scoured and transported either to washing vats or to any other section desired.

Advantages of the System. The makers claim the following advantages for their nitration system :

(1) The entire volume of acid comes into contact with the material to be nitrated, "the proportion between acid and material to be nitrated being thus more economical." The nitration phases are more energetic and rapid, while the yield from the acid is superior to that from other nitration systems.

(2) The composition of the acid mixture is always constant.

(3) A nitrated product of homogeneous composition is obtained, accompanied by a superior yield.

Information concerning the working of the Nitration Turbine.— Selwig and Lange's nitration turbine is made in two designs, of which the following are particulars :

Number	External diameter of the cage	Depth of the cage	Capacity		Capacity for cotton	Number of revolutions per minute	Power required in H.P.	
			of the cage	of the case			for starting	during the operation
	metres	millimetres		about	kilos	about		
I.	1·000	380	250′	375–400′	11–12	10 0	8–9	2–2·3
II.	0·850	360	175′	255′	7–8	1150	6–7	1·5–1·7

The time necessary for a complete nitration operation is from 55 to 60 minutes; per day of ten hours' work the maximum output is:

With the smaller design : $8k \times 11 = 88$ kilos. of cotton.
„ larger design : $12k \times 10 = 120$ „

The makers guarantee for the celluloid manufacture 160 per cent. yield with cotton and 130 per cent. with paper.

The following return gives the displacement of a nitration turbine:

Breadth = 3 to 3·20 metres; depth = 6·50 to 8 metres.

The premises actually devoted to the nitration, which are separated by a partition from the section containing the exhausters and the power gearing should be at least 6 to 8 metres square and 4·5 to 6 metres high.

To sum up. This process presents certain advantages over all those previously described.

We have ourselves tested this process under the following conditions:

The cellulose for nitration was in the form of paper from cotton fibre weighing 18 grammes per square metre. This paper was passed through the tearing-machine before immersion in acid, 5 kilogrammes being nitrated at each operation.

In the Table below are summarised the several particulars of each trial.

After each nitration the reduced centesimal composition of the sulphonitric mixture was restored by means of fresh acid to that existing before nitration. In this way the bath content in water and acids (sulphuric and nitric) did not alter during repeated operations.

Number of the trial	Centesimal composition of the Sulphonitric mixture			Number of operations	Weight of paper unwound	Mean temperature during nitration	Average duration		Weight of dry nitrated paper	Percentage yield
	HNO_3	HSO	HO				of the nitration	of the operation		
					kilos	deg.	minutes	hr. min.	kilos.	
I.	14·65	66·30	19·05	20	100	22	24	59	134·5	134·5
II.	15·23	65·94	18·83	20	100	19	23	60	136·8	136·8
III.	14·18	67·06	18·76	20	100	20	27	60	133·7	133·7
IV.	16·01	64·34	19·65	19	95	21	30	1 7	132·5	139·4
V.	13·96	68·11	17·93	18	90	23	30	1 11	119·1	132·3
VI.	15·07	65·51	19·42	20	100	23	31	60	135·8	135·8
VII.	15·84	62·91	21·25	21	105	21	29	57	145·6	138·7
VIII.	15·39	65·60	19·01	18	90	23	28	1 12	123·4	137·1
IX.	14·88	66·40	18·72	21	105	25	27	58	141·4	134·7
X.	15·71	66·31	20·98	20	100	24	29	60	138·2	138·2
XI.	13·80	66·45	19·75	20	100	24	30	60	131·8	131·8
XII.	14·55	66·92	18·53	20	100	22	32	60	134·5	134·5
XIII.	14·93	66·38	18·69	19	95	25	28	1 7	128·4	135·1

The objection to this apparatus is that of requiring a rather considerable, and therefore expensive, installation. For producing continuously 1000 kilos. of nitrocellulose in twenty-four hours (nitrating paper similar to that which has

served in the above trials), seven to eight centrifugalisers are necessary, each giving an average yield of 134 per cent.

Moreover, the makers have projected a new design, more especially destined for the celluloid trade, and capable of giving a much greater daily output—viz., "The Standard," 1909. The dimensions of the apparatus are as follows :

External diameter of cage	1200 mm.
Height of cage	570 ,,
Capacity for cotton	20 kg.
Quantity of acid up to 80 mm. below edge of cage	700 litres
Number of revolutions per minute	850
Power necessary { for starting	10 h.p.
Power necessary { during a normal operation	2·25 h.p.

The capacity of the charge being 20 kilogrammes and the duration of the complete operation about fifty-five minutes, the same calculation as the one preceding indicates that one apparatus will nitrate 220 kilogrammes per day, and, admitting a yield of 134 per cent. as the result of our previously quoted trials, we may expect 295 kilogrammes of nitrated paper per day. For producing 1000 kilogrammes of nitrocellulose per day, three to four turbines would suffice instead of seven to eight. From this the makers estimate the cost of installation to be reduced 60 per cent.

The Figure below represents Selwig and Lange's nitration turbine, design 1909.

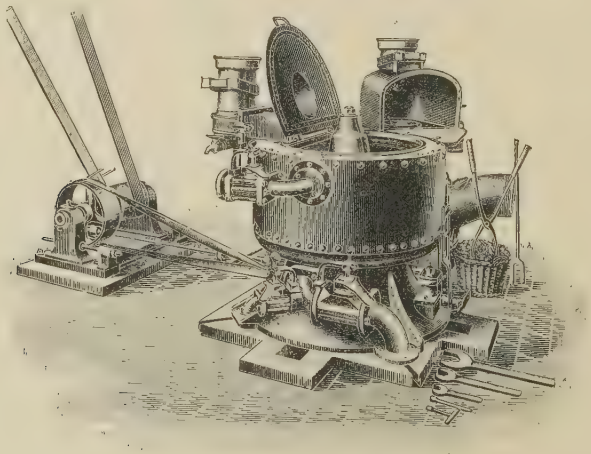


Fig. 14. Turbine Design 1909.

One of the advantages of these machines lies in the good hygienic conditions and the security attached to their working. In celluloid manufacture they are used by La Société Planchon, La Société Cines, La Bellignite, the Rochester Kodak Co., and in several German works.

In the latest installations the paper, instead of being torn up, is unwound into the turbine from an automatic roller electrically driven. The parts of

this machine exposed to acid contact or to acid fumes are of aluminium; the steel portions, the motor, etc., are enclosed in aluminium cases. One such unwinding machine can serve 4 turbines.

Morane's Process. A nitration turbine is used in this process formed of a plate D, on which is bolted a cage E. The whole is carried by a vertical shaft B, driven by the pulley C. (Fig 15.)

The cage is formed of a base F, and two concentric walls, G, H (Fig. 16).

The inner wall is perforated throughout, while the wall H, which is entire, only allows the passage of liquid by overflow.

Between the walls G H are metallic plates Z of helicoidal form which start from the bottom and meet at the top of the annular space formed by the walls G H in the upper part of the cage.

The apparatus is surmounted by a hood I, communicating with an exhaust pipe which draws away the fumes evolved during the operation into a condensing tower.

Two doors P provide for the working and inspection.

To accomplish the nitration, the exhaust is set working, the inlet acid tap is turned on into the cage, and when the latter is sufficiently full the tap is closed and the cage run at a low speed.

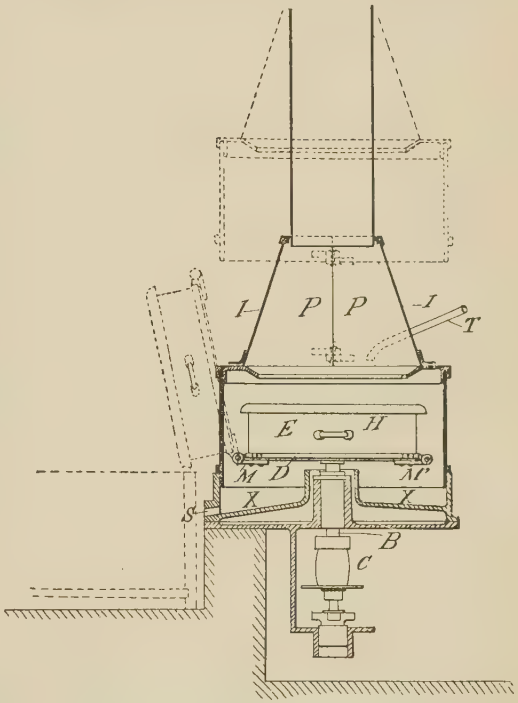


FIG. 15. Morane's turbine.

The operator introduces the cotton through the doors P, carefully ensuring its immersion by means of a rod. After the immersion has continued long enough, the rotation of the cage is accelerated until the maximum speed is attained.

The liquid, under the influence of centrifugal force, passes through the perforations of the wall G, follows the helicoidal plates to overflow at O, and falls back on to the draining plate X, from which it is conducted by the pipe S into a suitable receiver.

The rotation of the cage is stopped after a draining of some minutes, and the nitrocellulose withdrawn by means of the arrangement shown in Fig. 15, which permits of rapid discharge. In this arrangement the cage is movable,

and the hood I may be raised so as to allow the cage to be tilted about an axle. For this purpose the cage is jointed to the tray D by a hinge M, and is maintained during the tilting operation by similar hinges M′.

Other nitration turbines. There are also in use the nitration turbine constructed by the Braunschweigische Maschinenbau Anstalt, of Brunswick

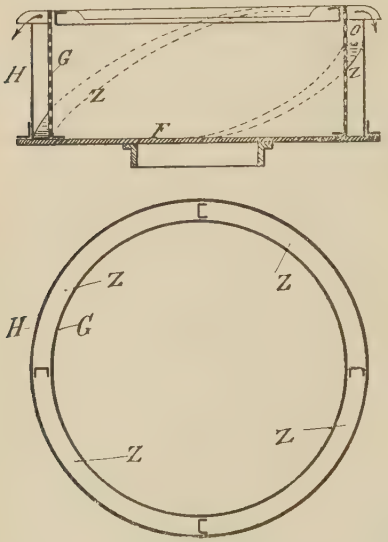


FIG. 16. Morane's turbine. Cage.

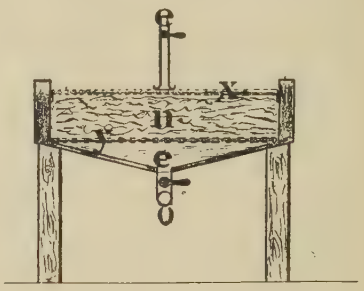


FIG. 17. Thomson's apparatus.

e Inlet water-pipe.
x and *y*. Perforated plates.
n. Space in which the paper to be nitrated is placed.
c. Basin for reception of acids.
o. Tap for withdrawal of acid after nitration.

(Germany); the turbine of the Brothers Heine, of Viersen (Germany) (German patent 81417).

We do not believe it necessary to enter into further details on the subject of turbines. The principle involved in them is always the same, and descriptions of the machines may easily be obtained from the makers or from the patents.

Thomson's Process. This is based on the following principle:

If in a receiver, furnished beneath with an outlet pipe, a sulphonitric mixture for bringing about the nitration be placed, and then water be added above this acid mixture without causing disturbance, the water will be completely separated from the part containing the cellulose undergoing nitration, and when the latter process has proceeded sufficiently the acid may be drawn off and replaced by the water, which thus washes the paper.

Description of the apparatus. The latter is made up of a lead vessel enclosed in wood, of cylindrical form and small height, whose base terminates in a conical part. At the bottom of the cone is a stout tap for withdrawing the acid.

Inside the apparatus are two stone circular slabs 5 millimètres thick and pierced with holes. The first perforated circle is fixed at the intersection of the cone and cylinder, and serves to retain the cellulose during the withdrawal of the acid.

The second circle is placed a short distance from the upper edge of the apparatus, and is surmounted by an adjoined piece upon which may be placed a pipe conveying the water destined for washing.

Finally, an unwinding apparatus and a paper tearer complete the nitration outfit.

The modus operandi of the apparatus. We commenced at the very outset by closing the outlet tap, then adding the sulphonitric mixture so as to be flush with the lower edge of the upper perforated plate, after allowing for the volume to be taken up by the cellulose.

The nitration then commences, care being taken to work as briskly as possible and to avoid forming lumps.

Immediately the immersion of the cellulose is made, the upper plate is lowered, and from the water inlet a small quantity of water is introduced which spreads over the plate forming a layer, and this, after filling up the plate holes, covers the whole entirely. Disturbance must be avoided, since heat would be generated by contact with the acid, entailing decomposition. The nitration is conducted with special regard to the temperature of the bath.

The nitration being accomplished, the outlet tap is slightly opened, the acid is drawn off, and the water-tap carefully opened. The flow of the latter is regulated so as to enter at the same rate as the acid runs away.

The acid is collected in different receivers; by means of a hydrometer the variation in density of the acid mixture is followed, and the acid portions separated according to their density.

When all the acid has been withdrawn, the washing is completed and the nitrocellulose placed in the washing vat.

This process presents some real advantages:

(1) Absence of nitrous fumes during the nitration period.
(2) Fractionation of analogous portions according to composition.
(3) Direct washing of the nitrated cellulose.

There is a reverse side, however; the working of the apparatus is very delicate, and though the manipulations of ordinary nitration are avoided, yet it is very uncertain owing to difficulties in carrying out the operations.

Immediately a moderate eddy is brought about between the mixture of neat acid and the water, a partial heating is produced.

We have tested this nitration process, which finds application in England.

The apparatus used by us was 1·20 m. in diameter; the height of the cylindrical part was 250 millimètres, and the depth of the cone at the centre from the intersection of the cylindrical part was 10 centimètres. The escape tap was of aluminium, mounted on a two-inch pipe also of aluminium. The water inlet pipe was half an inch.

Finally, the apparatus was mounted on a wooden frame, one metre in height, and covered with thin sheet lead. Thus comprised the apparatus had a capacity of about 275 litres.

At each operation 4 kilogrammes of paper, weighing 17 grammes per square metre, were unwound.

We allowed 100 kilogrammes of sulphonitric mixture per kilogramme of paper.

The time for unwinding was 10 to 12 minutes, according to the test; the duration of nitration was 25 minutes. Finally the time for running off the acid varied from 45 to 60 minutes.

Below are the results of three trials chosen from a large number of others :

Trial No. 1.

The Sulphonitric Mixture Employed.

Amount of the acids employed.		Density of the Sulphonitric mixture	Centesimal composition of the mixture			Content per weight of mixture	
By weight	By volume		HNO_3	H_2SO_4	H_2O	HNO_3	H_2SO_4
400 kil.	235 lit.	1·701	13·49	66·83	19·68	53·960 k.	267·320 k.

Temperature of mixture 24° C.

Sulphonitric Mixture Recovered.

Samples recovered	Amount of acids recovered		Density of the mixture	Centesimal composition of the mixture			Content by percentage weight	
	By weight	By volume		HNO_3	H_2SO_4	H_2O	of HNO_3	of H_2SO_4
	kilos.	litres					kilos	kilos
1	315·000	182 000	1·735	12·28	67·18	20·54	38·682	211·617
2	60·000	37 000	1·622	11·75	63·21	25·04	37·050	37·926
3	13·000	8·500	1·493	11·58	56·39	32·03	1·505	7·330
4	6·000	8·750	1·483	11·12	52·65	36·23	1·445	6·845
5	6·000	4·400	1·364	10·67	48·57	41·06	0·640	2·896
6	6·000	4·500	1·332	9·20	43·28	47·43	0·557	2·596
7	6·000	4·400	1·363	8·89	36·63	55·48	0·533	2·137
8	5·500	4·300	1·278	7·07	26·71	66·22	0·388	1·469
9	5·500	4·700	1·169	4·89	17·40	77·71	0·268	0·957
10	12·000	11·300	1·062	2·12	6·73	91·15	0·254	0·810
11	11·000	11·000	1·000	0·63	2·19	97·18	0·069	0·240
12	22·500	22·600	0·996	0·16	0·81	99·03	0·036	0·182
13	22·000	22·300	0·988	0·08	0·31	99·61	0·017	0·068
14	50·000	51·000	0·981	0·04	0·08	99·88	0·020	0·040
15	45·000	45·500	0·987	0·03	0·03	99·94	0·013	0·012
16	45·000	45·600	0·985	traces	0·02	99·99	—	0·009
17	46·000	46·100	0·995	—	0·01	100·00	—	0·004
18	230·000	230·000	1·000	—	0·02	100·00	—	0·004

Trial No. 2.

The Sulphonitric Mixture Employed.

Amount of acids employed		Density of the Sulphonitric mixture	Centesimal composition of the mixture			Contents by weight of the mixture in	
By weight	By volume		HNO_3	H_2SO_4	H_2O	HNO_3	H_2SO_4
400 k.	235 l.	1·698	13·55	66·48	19·97	54·200 k.	265·920 k.

Sulphonitric Mixture Recovered.

Samples recovered	Quantity of acids recovered		Density of the mixture	Centesimal composition of the mixture			Content by weight in	
	By weight	By volume		HNO_3	H_2SO_4	H_2O	HNO_3	H_2SO_4
	kilos.	litres					kilos.	kilos.
1	400	235	1·586	11·48	59·69	28·83	45·92	238·76
2	24	18	1·357	8·96	38·44	52·60	2·15	9·22
3	260	250	1·021	0·88	3·01	96·11	2·20	7·52

Nitration temperature 25°. Duration of nitration 26 minutes.
Duration of acid withdrawal 53 minutes.

Trial No. 3.

The Sulphonitric Mixture Employed.

Amount of acids employed		Density of the Sulphonitric mixture	Centesimal composition of the mixture			Content by weight of the mixture in	
By weight	By volume		HNO_3	H_2SO_4	H_2O	HNO_3	H_2SO_4
400 k.	235 l.	1·700	13·63	66·59	19·78	54·520 k.	266·360 k.

Sulphonitric Mixture Recovered.

Samples recovered	Quantity of acids recovered		Density of the mixture	Centesimal composition of the mixture			Content by weight in	
	By weight	By volume		HNO_3	H_2SO_4	H_2O	HNO_3	H_2SO_4
	kilos.	litres					kilos.	kilos.
1	400	235	1·584	11·55	59·49	28·96	46·16	237·96
2	24	18	1·358	8·79	38·64	52·57	2·10	9·27
3	260	250	1·009	0·89	3·15	95·96	2·22	7·87

Nitration temperature 24°. Duration of nitration 29 minutes.
Duration of acid withdrawal 48 minutes.

Nitration in pots. The process most in use, however, is that of nitration in pots.

This is especially the process employed by the Deutsche Celluloïd Fabrik, of Leipzig, by the Rheinische Gummi und Celluloïd Fabrik, of Neckarau (Mannheim), and by several French firms.

The Deutsche Celluloïd Fabrik nitrates paper or cotton.

The sulphonitric mixture is compounded in a pan in the ratio of about $\frac{2}{3}$ H_2SO_4 of 96 per cent. monohydrate and $\frac{1}{3}$ HNO_3 containing 42 per cent monohydrate. This mixture is conveyed by pipes into nitration pots of about 100 litres content, into which is introduced the paper or cotton to be nitrated. Seven to eight kilogrammes of acid per kilogramme of cotton to be nitrated are allowed, and 10 kilogrammes per kilo. of paper.

The duration of nitration is about 1 hour for paper and about 2 hours for cotton. Afterwards the sulphonitric mixture is run off into tanks where it is regenerated.

The recovery of the acid contained in the nitrocellulose is accomplished, as we shall see later, by placing the nitrocellulose in hydro-extractors, or by submitting it to the action of a hydraulic press.

This firm also nitrates with Selwig and Lange's turbine.

The Rheinishe Gummi und Celluloïd Fabrik, of Neckarau (Mannheim), also carry out nitration in pots, but they only employ paper. The temperature of the acid is rather high, and the mixture contains a large proportion of nitric acid having 48 per cent. monohydrate.

We have described many different nitration processes, and while some of these are not employed industrially, yet they may suggest useful ideas to our readers. We now pass on to the rationale of nitration.

CHAPTER IV

THE RATIONALE OF NITRATION

NITRATION

Conditions for a good nitration. It is necessary for securing a good nitration to have :

(1) A suitable white and dry cellulose.

The paper should be tested on its arrival and its condition noted.

(2) Acids as pure as possible and of the desired strength.

The selection of acids has already been noted.

We recommend the use of paper made from cotton for nitration.

The weight of this paper should not exceed twenty grammes per square metre.

A good paper is that supplied by Gunz, weighing eighteen grammes per square metre, and costing from 106 to 110 francs. The price is perhaps a little high, but this paper has given us excellent results.

Moist paper should carefully be avoided ; for greater security it is well to prepare a building heated to about 50° C. for storing the paper before use. This temperature, which is expensive, need not be attained, but the drying chamber for the paper may be heated to 24° or 25° C. by means of waste steam.

Nitration. We have previously mentioned that nitration baths are exceedingly numerous. For economic nitration it is necessary to use the least possible amount of sulphonitric mixture per kilogramme of paper and to have the weakest centesimal composition possible, so as to reduce the net cost to a minimum.

Nevertheless, the product should be capable of giving good results. The use of 100 kilogrammes of sulphonitric mixture per kilogramme of paper to be nitrated may be recommended.

As composition of the bath :

Nitric Acid of 40° B.
Sulphuric Acid of 66° B.

Per kilogramme of paper the necessary minimum is :

Nitric Acid, 4 kilogrammes having 61·5 or 61·6 per cent. of monohydrate.

Sulphuric Acid, 9·3 kilogrammes having a minimum of 93·5 per cent. monohydrate.

We therefore have 13·3 kgr. of a mixture which should have a minimum density of 60·2° at 15° C.

The best nitration temperature is 25° C. and this should vary very little during the operation.

The duration of the nitration with this mixture should be thirty minutes, not including the five minutes required for unrolling the paper.

Washing. When the acids are not to be recovered washing takes place immediately the nitration is over.

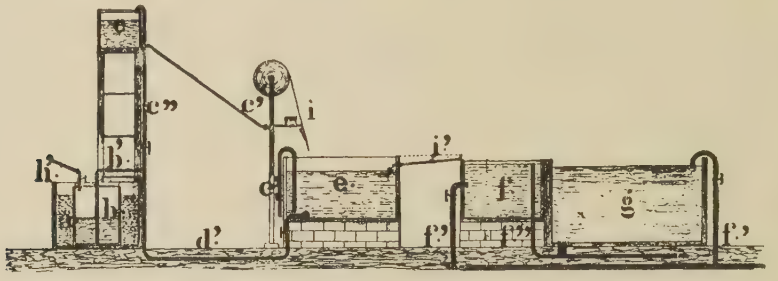


FIG. 18. Ordinary nitration system without acid recovery.

Description.

a. Vat employed for heating or cooling the acid baths.
b. Vessel in which the sulphonitric mixture is prepared.
b'. Outlet pipe for the acid from pot b.
h'. Pipe for introducing compressed air.
c. Charged bath for feeding as the unrolling takes place.
c'. Pipe proceeding from the bath c to the place of unrolling.
i. Machine for wetting the unrolled paper.
c''. Pipe leading from the sulphonitric mixture to the bath c.
d. A paper reel.
d'. Supply pipe for the nitration bath.
e. Nitration bath.
e'. Siphon for emptying the nitration bath.
i'. Draining board.
f. Glass lined vat in which the first washing of the nitrated paper takes place.
f'. Water inlet pipe.
f''. Outlet pipe for acidified water.
g. Bath for washing the nitrocellulose.

The latter process is carried out by vigorously plunging the paper into a large volume of water which is constantly being drawn off. On account of the large proportion of acid contained in the paper a vat capable of resisting acid attack must be employed for the first steeping. Generally these vats are of lava stone (volvic), or lined with glass.

The paper is next placed in a wooden washing vat where it is well treated with running water.

This non-recovery system is naturally little used on account of the enormous loss in acid.

Nitration yields. We have seen previously when studying the various nitration systems that the yields were extremely variable.

In the trials we have made on the use of the sulphonitric mixture recommended in this chapter on "The Rationale of Nitration," we have obtained, after

long experience, 148·610 kgr. to 152·700 kgr. of nitrated paper from 100 kilogrammes of unwound paper.

With this nitration bath 149 to 149·5 per cent. may be taken as a good yield.

RECOVERY OF THE ACIDS

For each kilogramme of paper 13·300 kgr. of sulphonitric mixture are necessary, and if washing immediately follows nitration the greater part of the acid is lost, only that being utilised which is fixed by the paper to form nitrated cellulose. Various methods are therefore in use to diminish the loss of nitric and sulphuric acids.

Among the various processes employed for recovering the acid retained in the paper, we shall quote:

(1) *Pressing.* Formerly iron rakes were used fixed to hollow handles, through which passed a bar of smaller diameter also carrying a rake at its extremity.

This rake was worked in the following way:

Taking the nitrated paper proceeding from the sulphonitric bath by means of the first rake the nitrocellulose is pressed by means of the second, which is moved up to the first. By means of a key placed in holes prepared along the handles the paper is maintained in a pressed condition.

Other firms employ an analogous system, but possessing a clamping-screw.

These systems, which all exert very small pressures and in consequence express only very small quantities of acid, require slow and laborious work on the part of the staff.

The hydraulic press was therefore devised and this is always in use in works.

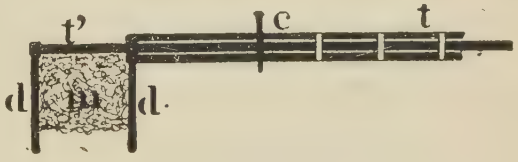


Fig. 19. Pressing Rake.

t. External hollow tube.
t'. Internal solid tube
c. Pins for fixing both tubes.
d. Teeth on the rake.
m. Pressed nitrocellulose.

The above process is very similar to that used in the oil industry. As may be seen from the Figure shown on page 50, it is composed of a cylinder carrying a plate whose edges are provided with small gutters.

The plate is guided by two pillars supporting the frame of the press. Above this piece, and fixed, is the plunger which just plays into the cylinder supported by the plate. The piston is made of iron and is solid; the cylinder, constructed of steel 5 to 6 millimètres thick, is perforated with numerous holes.

The nitration pots are placed alongside the press. When the nitration has been accomplished, the nitrocellulose is allowed to drain slightly upon a perforated floor of copper or aluminium, then placed in the cylinder of the press.

When the latter is full, pressure is applied to the contents; the plate ascends, carrying the perforated cylinder into which the piston fits. Under the great pressure produced (150 kgr. per square centimetre) the acid contained in the nitrocellulose is expressed and falls upon the plate of the press, where the gutters convey it to a pipe which in turn conducts it to a tank.

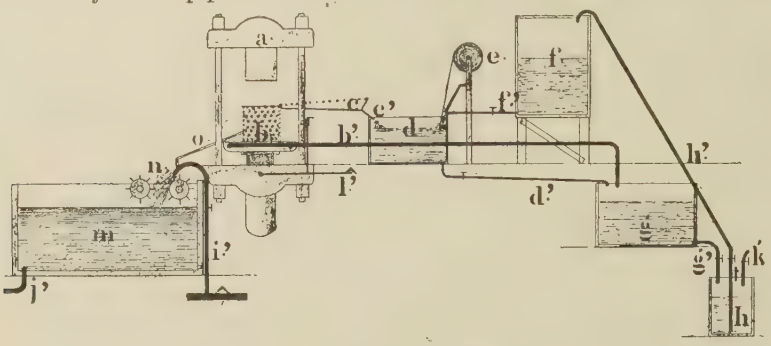


FIG. 20. Recovery by Pressing.

a. Plunger of the press. b. Perforated cylinder.
b'. Outlet pipe for the acid expressed from the nitrocellulose.
c. Draining floor.
c'. Acid return pipe to the nitration bath.
d. Nitration bath. e. Paper reel.
f. Tank for the sulphonitric mixture to be used in the nitration.
f'. Pipe for conveying the sulphonitric mixture to the nitration bath.
d' Acid withdrawal pipe, used for emptying the nitration bath and for conveying the acid to the tank g.
g. Tank into which the acid proceeding from the nitration bath and press is collected.
g'. Pipe conveying the mixture recovered in g to the pot h.
h. Pot used for the return process. k'. Compressed air pipe.
h'. Pipe feeding the bath with fresh sulphonitric mixture.
m. Washing vat for the nitrated paper.
n. Tearing machine for the cakes of nitrated paper.
i'. Water inlet pipe. j'. Water exit pipe.

By using the hydraulic press, there may be recovered from 6·500 to 7 kgr. of sulphonitric mixture per kilogramme of nitrated paper.

Unfortunately the nitrocellulose so pressed takes the form of a cake, which adhering to the perforated cylinder is very difficult to remove. This inconvenience may be obviated by using a cylinder in two sections, maintained upon the plate by corner irons. Nevertheless, the cake obtained is so compact that it is necessary to pass it into a tearing machine, thus augmenting the manual labour and occasioning loss of nitrocellulose, which is reduced to pulp.

(2) *Hydro-extraction of the nitrocellulose.* The method of recovery by hydro-extraction is the best.

The paper, being nitrated, is placed in an hydro-extractor, where it is freed from the sulphonitric mixture by centrifugal force, which projects the acid to the periphery of the apparatus and so allows it to be collected.

The centrifugalisers in actual use are driven underneath by means of a shaft which carries a cage usually of steel. This cage is perforated by numerous holes

through which the acid may run away. This is enclosed in a case having a funnel-shaped bottom. Usually the case is provided above with a hood through which escape the fumes from the sulphonitric mixture returned by the nitrated paper. Finally, the top of the cage is closed by a lid.

These hydro-extractors make 800 to 900 revolutions per minute, and generally require from 7 to 10 horse-power. The power is moreover very variable, and this variation does not admit of employing ordinary driving gear with success. Belt-slipping during rotation can hardly be avoided, since a machine having a large moment of inertia is connected with a shaft turning at full speed. The most elegant solution is to drive the centrifugaliser direct by an electric motor stationed below the pan and connected to the same shaft. All lateral strain is thus avoided. The speed of rotation of the machine allows a good yield from the motor, and the maximum speed for which the apparatus is constructed cannot be exceeded, thus avoiding risk of explosion. Special electric motors have been constructed which never spark between the collecting brushes, and whose starting is performed by rheostats avoiding overheating of the motor.

The management of these machines is simple, nevertheless their working is fairly delicate. The official in charge should be careful in loading the cage to distribute the layers of nitrocellulose accurately, otherwise should the cage be not charged uniformly irregular oscillations are produced during rotation, and not only is the acid expulsion troublesome but the cage does not turn properly, thus wearing away the pivot unequally and causing the apparatus to sway after a short period.

By means of the centrifugaliser 5 to 6·5 kgr. of acid per kilogramme of paper may be recovered.

Below are given the results of trials which we have carried out on the recovery of the sulphonitric mixture by means of the hydro-extractor. These trials were conducted with 5 kilogrammes of paper. The nitration bath employed in the trials had the following composition :

HNO_3	18·52 per cent.
H_2SO_4	65·72 „
H_2O	15·74 „

This bath was obtained by mixing :

4 kgr. nitric acid containing 61·6 per cent. of monohydrate.

9·3 kgr. sulphuric acid containing 94 per cent. of monohydrate.

The paper for nitration weighed 17 grammes per square metre.

The unwinding occupied 6 to 6½ minutes ; the duration of nitration was 28 minutes.

Each nitration pot contained :

20 kgr. nitric acid containing 61·6 per cent. of monohydrate.

46·500 kgr. sulphuric acid containing 94 per cent. of monohydrate.

5 kgr. of paper weighing 17 grammes per square metre.

After nitration, the paper was hydro-extracted in a centrifugaliser making

832 revolutions per minute. Nine to ten minutes were necessary for charging the 5 kilogrammes of nitrocellulose (or more correctly 6 kilogrammes, taking account of the yield). The duration of hydro-extraction was from five to six minutes.

After straining 30·500 kgr. of sulphonitric mixture, or 6·100 kgr. of acid per kilo. of paper unwound, were collected.

The recovered mixture had the following centesimal composition:

HNO_3	9·45 per cent.
H_2SO_4	69·70 „
H_2O	20·85 „

Therefore in the 30·500 kilogrammes of sulphonitric mixture recovered there were:

$$HNO_3 = \frac{9{\cdot}450 \times 30{\cdot}5}{100} = 2{\cdot}882 \text{ kgr.}$$

$$H_2SO_4 = \frac{69{\cdot}70 \times 30{\cdot}5}{100} = 21{\cdot}258 \text{ kgr.}$$

$$HO_2 = \frac{20{\cdot}85 \times 30{\cdot}5}{100} = 6{\cdot}359 \text{ kgr.}$$

RESETTING THE NITRATION BATHS

We have just seen the condition of a recovered bath which has served for one nitration. Under what conditions should it be employed for a second nitration?

During nitration the following have been used respectively:

HNO_3	2·463 kgr.	× 5	=	12·315 kgr.
H_2SO_4	8·740 „	× 5	=	43·700 „
H_2O	2·093 „	× 5	=	10·465 „

For a second nitration under the same conditions there are, therefore, necessary: 66·500 kgr. of acids less 30·500 kgr., *i.e.* 36 kilogrammes of a mixture containing respectively:

HNO_3	H_2SO_4	H_2O
12·315 kgr.	43·700 kgr.	10·465 kgr.
2·882 „	21·258 „	6·359 „
9·433 „	22·442 „	4·106 „

By means of fresh acid this composition may easily be obtained. As far as possible sulphuric and nitric acids should be employed containing the maximum percentage of monohydrate, so as to reduce to a minimum the increase by weight of the mixture recovered. This is the operation known as the "resetting" (remontage) of the baths.

The resetting of the nitration baths is an important operation in the nitration of celluloses.

After nitration the bath is richer in water. Its sulphuric acid percentage

has increased, while its nitric acid content has diminished. This bath has been termed the "old bath." To re-establish the initial bath, *i.e.* to reset to the new bath, it is necessary to add a calculated quantity of sulphonitric mixture to the old bath.

The initial bath is a fixed stock started at the commencement of the works, and from time to time a portion only of the bath is sold because of the increase in organic matters. All the factors involved in properly resetting the bath by the use of acid mixtures of minimum cost will thus be comprehended.

We will now reproduce an interesting study of the conditions necessary for obtaining these mixtures, on the influence of the different variables, and upon the possibility of establishing a bath capable of easy readjustment. This study, due to M. Clément, has been published in *Le Caoutchouc et la Gutta-Percha* (May 1909).

General formulæ for resetting baths. The starting bath, *i.e.* the new bath, is made up of sulphuric acid, nitric acid, and water.

Let $\begin{cases} x \text{ be the percentage proportion of } H_2SO_4 \\ y \quad \text{,,} \quad \text{,,} \quad HNO_3 \\ z \quad \text{,,} \quad \text{,,} \quad H_2O \end{cases}$

We have obviously $x + y + z = 100$.

After nitration the old bath has for its composition:

$$\begin{cases} x' \text{ per cent. } H_2SO_4 \\ y' \quad \text{,,} \quad HNO_3 \\ z' \quad \text{,,} \quad H_2O \end{cases}$$

Similarly, $x' + y' + z' = 100$

(The nitrous vapours of both new and old baths are reckoned as nitric acid.)

The problem is to add sulphuric and nitric acids to the old bath in amounts sufficient to adjust the contents x', y', z' to x, y, z. In addition, we have a liquid whose water proportion is too great. By adding to it a second liquid of lesser content, the mixture will possess a lower water percentage than the first, this being a simple rule for mixtures.

Let s be the strength for the sulphuric acid employed for resetting, *i.e.* the weight of H_2SO_4 contained in 100 grammes of this acid.

Let n be the strength of the nitric acid, *i.e.* the percentage proportion of HNO_3.

Again, let S be the weight of sulphuric acid of strength s necessary to reset 100 grammes of the old bath (or 100 parts by weight); N the weight of nitric acid of strength n required for the same purpose.

Therefore let us observe what happens when 100 grammes of the old bath are taken and S and N grammes added to it.,

The weight of H_2SO_4 in the mixture is: $x' + \frac{Ss}{100}$

The weight of HNO_3 in the mixture is: $y' + \frac{Nn}{100}$

Total weight of the mixture is: $x' + y' + z' + S + N = 100 + S + N$.

Now, after the addition of S and N, we must have a bath whose percentage in H_2SO_4 is x, and in HNO_3 y; therefore we must have:

$$x = \frac{\left(x' + \frac{Ss}{100}\right)100}{100 + S + N} = \frac{100x' + Ss}{100 + S + N} \tag{1}$$

$$y = \frac{\left(y' + \frac{Nn}{100}\right)100}{100 + S + N} = \frac{100y' + Nn}{100 + S + N} \tag{2}$$

It only remains to solve the equations (1) and (2) in order to find N and S. The solution is simple:

By division we have: $\frac{x}{y} = \frac{100x' + Ss}{100y' + Nn}$, from which we deduce:

$$Ss = \frac{x}{y}(100y' + Nn) - 100x'$$

Replacing Ss by this value in (1), it becomes:

$$x = \frac{\frac{x}{y}(100y' + Nn)}{100 + \frac{x}{ys}(100y' + Nn) - \frac{100x'}{s} + N}$$

from which we easily deduce:

$$N = \frac{100\left[y\left(1 - \frac{x'}{s}\right) + y'\left(\frac{x}{s} - 1\right)\right]}{n\left(1 - \frac{x}{s}\right) - y} = \frac{100[s(y - y') + xy' - x'y]}{n(s - x) - ys}$$

and

$$S = \frac{100\left[x\left(1 - \frac{y'}{n}\right) + x'\left(\frac{y}{n} - 1\right)\right]}{s\left(1 - \frac{y}{n}\right) - x} = \frac{100[n(x - x') + x'y - xy']}{s(n - y) - nx}$$

Such are the two formulæ by which the nitration baths may be readjusted. x, y, z, x', y', z', s and n are replaced by their values in these formulæ. We shall next examine the results.

DISCUSSION OF THE FOREGOING FORMULÆ.

N and S are functions of the variables s, n, x' and y'.

s and n vary but slightly. The acid proportions may be very constant. We shall vary them in order to study the influence of the acid concentrations upon the values of S and N.

x' and y' vary according to the conduct of the nitration. In a well-established firm they are kept practically constant.

For the present there is no question of varying x and y, the initial contents of

the bath. Later, when seeking for a bath capable of easier adjustment, we shall vary them between certain limits.

I. STUDY OF THE VARIATIONS OF N.

(a) *n the only variable.*

By resetting our bath with mixtures containing nitric acids of different concentration and sulphuric acid of constant strength we shall see how N varies.

It is possible to make this study directly from the formulæ established, but in order not to argue solely with letters and not to be wearied by symbols which do not immediately respond to our intentions, we shall always take an example in these discussions.

Let us, therefore, construct a theoretical bath having the following data:

New Bath	*Old Bath*
$x = 60$	$x' = 60{\cdot}3$
$y = 20$	$y' = 19{\cdot}5$
$z = 20$	$z' = 20{\cdot}2$

The value found for N is: $N = \dfrac{100\,[s\,(y - y') + xy' - x'y]}{n\,(s - x) - ys}$

It is easy to see that N varies as a hyperbolic function of n.

The two asymptotes are: $N = o$ and $n = \dfrac{ys}{s - x}$

In the two following Tables the calculations are summarised.

The value of N is found with regard to n. These Tables are arranged for two values of s: (1) $s = 92{\cdot}5$; (2) $s = 97$ (see Fig. 21).

$s = 92{\cdot}5$

$$N = \frac{12{\cdot}25}{0{\cdot}325n - 18{\cdot}5}$$

n	N
o	$-0{\cdot}66$
.....	.....
56·9	∞
60	12·25
65	4·64
67·5	3·5
80	1·6
100	0·87
,,	,,

$s = 97$

$$N = \frac{14{\cdot}5}{0{\cdot}37n - 19{\cdot}4}$$

n	N
o	$-0{\cdot}74$
.....	.....
52·4	∞
55	15
60	5·17
65	3·11
70	2·23
80	1·40
100	0·82

The behaviour of the two functions (see the curves) is interesting. There exists one concentration of nitric acid such that readjustment with this acid is impossible. This is the concentration at the asymptotes $n = 56{\cdot}9$ or $52{\cdot}4$ in the foregoing cases. The acids contain too much water. It will be seen that the weight N lowers very quickly as n increases; hence the reason for the use of a concentrated nitric acid. In the first case N is lowered—for example, by 0·8 k. from $n = 70$ to $n = 75$, and only by 0·400 k. between 75 and 80.

We may also observe, and this is very important, that if s increases the curve is lowered entirely. The values of N for $s = 97$ are smaller than the corresponding values for $s = 92{\cdot}5$.

It is therefore necessary to use the most concentrated sulphuric acid possible. To a certain extent the dilution of the HNO_3 may be compensated by the con-

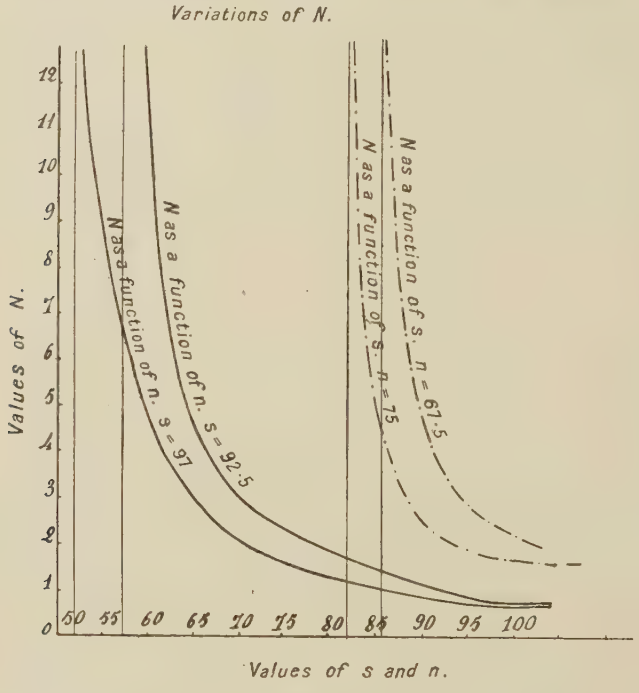


FIG. 21.

centration of the H_2SO_4. This may be readily seen from the curves by cutting them with a series of horizontals.

$s = 97$, $n = 70$, gives the same value for N as $s = 92{\cdot}5$, $n = 74$, or 2·2 k. The practical importance of these questions will thus be apparent.

Cost of the nitric acid. The price of nitric acid is a function of the concentration, as may be seen by consulting the following Table :

Density.	Degree Baumé.	n.	Price of 100 k.
1·300	33·3	47·49	24 „
1·400	41·2	65·30	33 „
—	—	—	—
1·425	43·5	70	40 „
1·440	44·1	74·68	58·50
1·480	46·8	86·05	80 „
1·500	48·7	98·1	88 „

There is no proportionality.

We shall show that every advantage is gained by resetting the baths with concentrated nitric acid, notwithstanding its higher price. It is understood that we use concentrated sulphuric acid, the price of which does not change with concentration (the acid $s = 99$ [1] may be procured for eight francs the 100 kilos., which is the price of the acid 95–96, etc.).

Let $s = 97$; therefore $N = 3$ kil. for 100 kilos. of the old bath, and $n = 65$. Price 0·99 fr.

Take $n = 70$; $N = 2{\cdot}20$ kil. Price 2 fr. $20 \times 0{\cdot}4 = 0{\cdot}88$ fr.

We have constructed on the curve opposite the price of N as a function of n, by utilising the prices given above (for $s = 97$). This curve presents a maximum and a minimum, but falls quickly when the concentration increases. (Fig. 22.)

Price Curve for N.

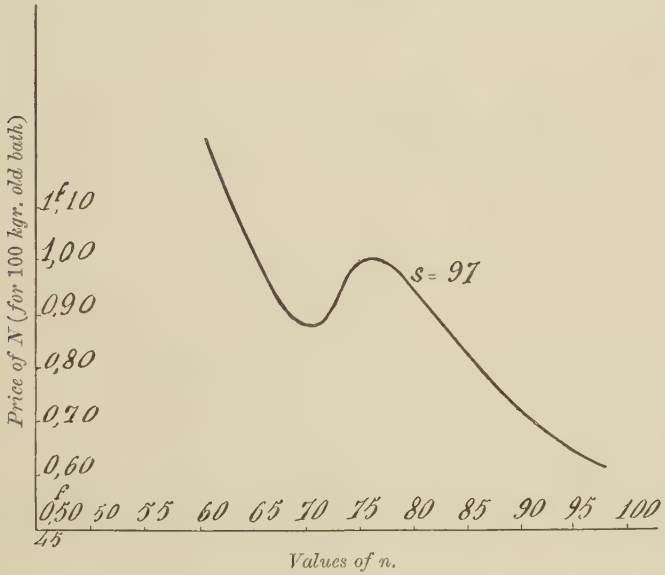


Fig. 22.

(b) *s the only variable.*

n is supposed constant. We shall study the variations of N when the baths are reset by employing sulphuric acids of varying strengths.

$$N = \frac{100\,[s\,(y - y') + xy' - x'y]}{s\,(n - y) - nx}$$

This is again a hyperbolic function. The calculation details are not given, but the results are summarised in the two following Tables. (*See* Fig. 21.)

[1] Made by the contact process.

$n = 67{\cdot}5$

$$N = \frac{0{\cdot}5s - 34}{0{\cdot}475s - 40{\cdot}5}$$

s	N
0	0·86
10	0·75
68	0
85·2	∞
87·5	9·10
90	4·88
92·5	3·60
95	2·92
100	2·28

$n = 75$

$$N = \frac{0{\cdot}5s - 34}{0{\cdot}55s - 45}$$

s	N
0	0·75
10	0·73
68	0
81·82	∞
85	4·6
90	2·44
95	1·80
100	1·60
„	„

The curves n fall much more rapidly than the preceding ones. The acid s between 95 and 100 should be utilised. As before, when n increases, N diminishes.

The only conclusion we shall draw from this preliminary study is, that the baths must be reset with concentrated acids. By employing concentrated sulphuric acid, we economise nitric acid; by using nitric acid of high concentration less is required and the cost of resetting diminished.

(2) VARIATIONS OF S.

(a) *Only n variable.*

The study of the variations of S does not present the same interest as that of N, since sulphuric acid is not an expensive product.

The value of S is: $$\frac{100\,[n\,(x - x') - xy' + x'y]}{s\,(n - y) - nx}$$

We shall assume S constant as before and study the variations of S as a function of the variable n. The calculations are made from the preceding bath.

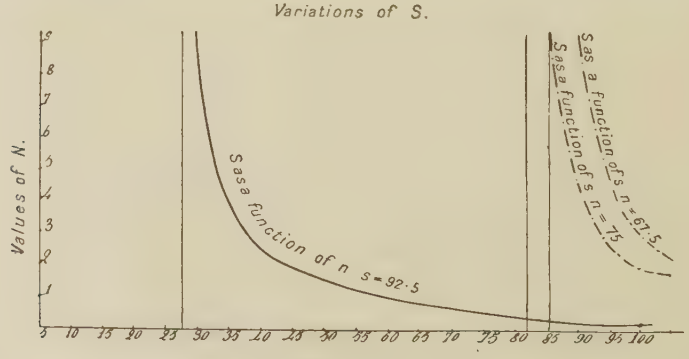


FIG. 23.

$s = 92{\cdot}5$

$$S = \frac{100\ (34 - 0{\cdot}2n)}{72{\cdot}5n - 1850}$$

n	S
25·51	∞
30	8·60
40	2·46
60	0·88
100	0.25
,,	,,

$s = 95$

$$S = \frac{100\ (34 - 0{\cdot}2n)}{75n - 1900}$$

n	S
25·3	∞
30	8
40	2·36
50	1·29
60	0·84
100	0·25

$s = 97$

$$S = \frac{100\ (34 - 0{\cdot}2n)}{77n - 1940}$$

n	S
25·1	∞
30	7·50
40	2·36
50	1·25
60	0·81
100	0·24

From the sole inspection of the Tables and curves, an immediate deduction may be made. The acids $s = 92{\cdot}5$ or $s = 97$ give practically the same results. The value of S falls very rapidly and for concentrations of n between 50 and 100 becomes very small.

S will not therefore detain us since the conditions which cause N to diminish equally decrease S.

(b) *s the only variable.*

The calculation Tables with the same baths are as follows:

$n = 67{\cdot}5$

$$S = \frac{20{\cdot}5}{0{\cdot}475s - 40{\cdot}5}$$

s	S
85·2	∞
90	9·11
95	4·44
100	2·92
,,	,,
,,	,,

$n = 75$

$$N = \frac{19}{0{\cdot}55s - 45}$$

s	S
81·81	∞
85	10·80
90	4·22
95	2·62
97	2·20
100	1·90

The diminution is especially important from $s = 95$ onwards and S falls when the strength of the nitric acid employed increases.

CONCLUSION.

Summing up the remarks made, the general conclusion from this group of studies is that;

The baths should be reset with concentrated acids. The greater the gain in sulphuric acid concentration, the less the consumption of nitric acid. The greater the concentration of the nitric acid, the less will be required and the decrease is not proportional.

Does a bath exist capable of easier renewal?

In order to continue the discussion commenced, we shall only vary the proportions of x and y the components of the bath. By this means we shall set up a series of baths and find which requires the minimum weights of S and N.

The latter baths will be those of easier renewal. Among them, however,

only a select few are of value, viz., those which will nitrate celluloses to the same degree and with the same nitrogen content.

Study of this variation.

(*a*) *Variations of N.* We have seen that: $N = \frac{100\,[s\,(y - y') + xy' - x'y]}{n(s - x) - ys}$

x being the variable.

Baths having the same water content and undergoing, during the nitration process, an equal variation of this content (through special physical conditions), nitrate theoretically to the same degree of nitrogen, as we have shown during the theoretical study of the nitration baths. The speeds of reaction, for example, probably change. Since we have made an examination of a theoretical nitration bath, we can apply the results previously announced (which have been theoretically established) to our investigation. The baths obtained shall be examined and, in the series found, practice only will determine those which give every satisfaction from the nitration standpoint (appearance of the nitrocellulose, speed of the reaction, &c. &c.). On the same grounds, the bath must satisfy the condition of easy renewal, and then a bath working normally will have been set up.

Let $z = 20$ correspond to the constant degree of nitration. The modulus of nitration, $z - z' = 0{\cdot}3$, for example.

$$x + y + 20 = 100. \quad \text{Therefore } x + y = 80.$$

$$x' + y' + 20{\cdot}3 = 100. \qquad x' + y' = 79{\cdot}7.$$

Suppose $x' = x + k$, and replacing x', y', y, by their values in N:

$$N = \frac{100\,[s\,(80 - x) - (79{\cdot}7 - x - k)] + x(79{\cdot}7 - x - k) - (x + k)\,(80 - x)}{n\,(s - x) - (80 - x)\,s}$$

Hence:

$$N = \frac{100\,[s\,(0{\cdot}3 = k) - 0{\cdot}3\,x - 80\,k]}{s\,(n - 80) + x\,(s - n)}$$

N varies again as a hyperbolic function of x.

The following are some results (*see* Fig. 24):

$s = 95$, $n = 70$, $k = 0{\cdot}2$

$$N = \frac{100\,(31{\cdot}5 - 0{\cdot}3x)}{25x - 950}$$

x	N
38	∞
40	39
50	5·5
60	2·45
70	1·31
90	0·34
100	0·09

$s = 98$, n 70, $k = 0{\cdot}2$

$$N = \frac{100\,(33 - 0\,3\,x)}{28x - 980}$$

x	N
35	∞
40	15
50	4·28
60	2·10
70	1·20
100	0·16
,,	,,

The fall is seen to be very rapid from the asymptote. It relapses into normal values of N for $x = 55$ or 60. N diminishes when the strength of the sulphuric

acid used for renewing the baths is increased, but for large values of x this diminution is small.

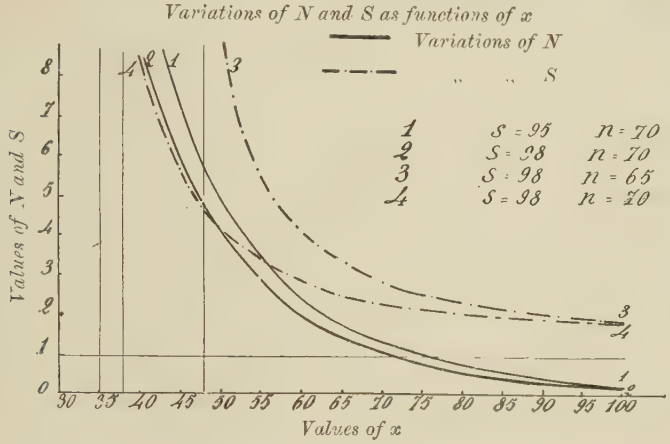

Variations of N and S as functions of x
Variations of N
" " S
1 S = 95 n = 70
2 S = 98 n = 70
3 S = 98 n = 65
4 S = 98 n = 70
Values of N and S
Values of x
0 1 2 3 4 5 6 7 8
30 35 40 45 50 55 60 65 70 75 80 85 90 95 100

FIG. 24.

Summing up, a bath rich in sulphuric acid is more economically renewed. Note that we must adopt a sulphuric acid content which will not impede nitration. In practice the values of x should be taken between 55 and 65.

Let us now examine the variations of S.

(*b*) *Variations of S.* If we replace x', y', and y by their values in the formula for S, we readily obtain :

$$S = 100\,\frac{80\,k + 0{\cdot}3\,x - kn}{s\,(n - 80) + x\,(s - n)}$$

Let us make the calculation for different values of N (*see* Fig. 24) :

$s = 98$, $n = 65$, $k = 0{\cdot}2$

$$S = \frac{3 + 0{\cdot}3x}{33x - 1470}$$

x	s
47·59	∞
50	10
55	5·60
60	4·10
80	2·30
90	2
100	1·70
∞	0·99

$n = 70$, $k = 0{\cdot}2$, $s = 98$

$$S = \frac{2 + 0{\cdot}3x}{28x - 980}$$

x	s
35	∞
40	10·68
50	4·28
60	2·85
80	2·06
90	1·88
100	1·07
"	"

These two curve types are particularly interesting; when the strength of the nitric acid for renewal increases, the curve quickly assumes the direction of its horizontal asymptote and S hardly alters for different values of x; S practically decreases no further when the sulphuric acid content increases. It was entirely otherwise with N. The results acquired for N are at the same time true for S.

GENERAL CONCLUSIONS.

We deduce as conclusions from this work :

(1) The renewal of the spent baths should be made with concentrated acids. If there is only a nitric acid of average concentration at disposal, economy may be exercised to a certain extent by increasing the strength of the sulphuric acid.

(2) Baths rich in sulphuric acid are more easily renewed. The sulphuric acid content of the baths should therefore as far as possible be increased, without however impeding nitration.

Let us observe further that the nitrocellulose, in spite of the hydro-extraction, carries away with it a certain amount of the sulphonitric mixture, and this is better taken from a bath rich in sulphuric, which costs less than from a bath rich in nitric.

The loss due to evaporation from baths rich in sulphuric acid (nitric acid) is less considerable.

From every standpoint it would be interesting to try the nitration of celluloses with baths rich in sulphuric acid (but containing always the same water content). An examination of the physical conditions would probably afford the solution.

INSTALLATION OF THE NITRATION WORKS.

To fix our ideas, we will next examine the installation of a nitration works in which 500 kilogrammes of paper are unwound per day. (Figs. 25 and 26.)

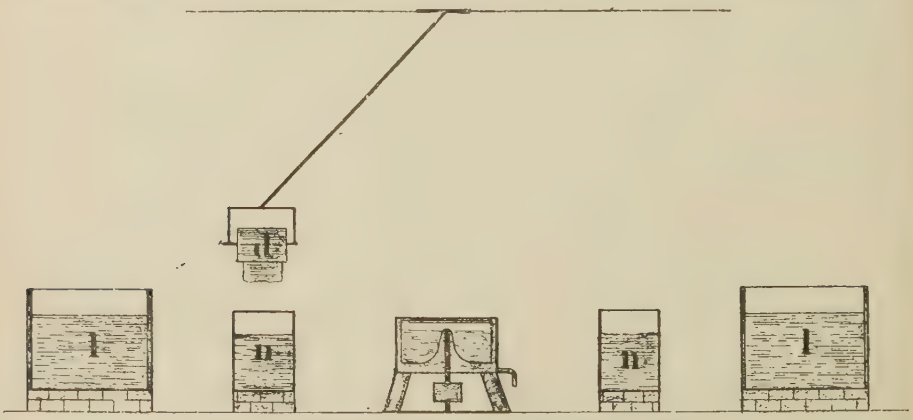


FIG. 25. Scheme of the nitration installation (section).

The nitration system employed includes acid recovery.

(1) *Nitration Pots.*

Generally 5 kilogrammes of paper per pot are nitrated.

The time necessary for complete nitration is :

Unwinding	10 minutes.
Nitration	30 „
Hydro-extraction	10 „

or a maximum of 50 minutes per pot.

There may therefore be nitrated during 10 working hours:

$$\frac{5 \text{ kil.} \times 600}{50} = 60 \text{ kgr. of paper.}$$

The calculation should be based upon a battery of 10 nitration pots. The dimensions of the latter are:

Diameter	800 mm.
Height	900 mm.

These pots have a tap at their base.

In Figures 25 and 26 the pots are placed in a circular battery, and the centrifugalisers are situated at the centre of the circle so formed. We recommend this arrangement as being the most practical from a management standpoint.

The centrifugalisers are two in number, whence it follows that they make 50 hydro-extractions per day.

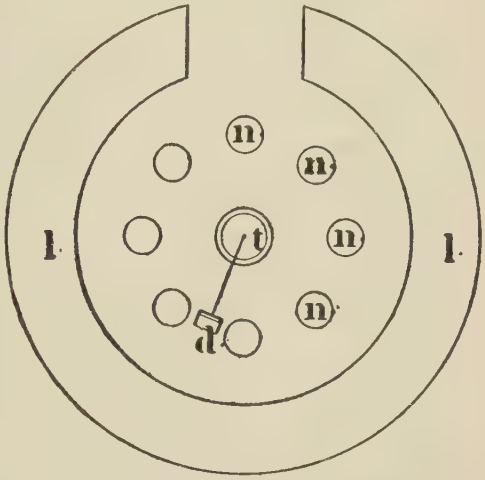


FIG. 26. Scheme of the nitration installation (plan).
n. Nitration pots.
t. Turbine for hydro-extracting the nitrated paper.
l. Vat for washing the nitrocellulose.

The wash vats, four in number, are placed externally; one serves to wash the paper immediately it comes from the hydro-extractor. The other three are connected together.

These vats have the following dimensions:

(1) *Vat for preliminary washing.*		(2) *Vats for the washing proper.*	
Length	1500 mm.	Length	5000 mm.
Breadth	1000 „	Breadth	2000 „
Height	900 „	Height	900 „

The nitration pots may also be arranged in two rows, the centrifugalisers being placed between the rows. The washing vats are then placed beyond the nitration pots.

In the battery arrangement of the nitration system a single unwinding apparatus serves the nitration pots; it includes a light framework fixed to the ceiling of the nitration chamber which, by means of a pivot, may be placed above the pots.

There should also be taken into account five tanks, each having a capacity of 12,000 litres, for storing the fresh and recovered sulphonitric mixtures.

One or two of these tanks should be jacketed so as to allow the acids to be heated or cooled.

An exhaust and an air compressor, with its store of compressed air, complete the installation.

CHAPTER V

THE BLEACHING OF NITROCELLULOSE USED IN CELLULOID MANUFACTURE

The bleaching of nitrocellulose resulting from the nitration of cotton or paper constitutes an important operation in the manufacture of celluloid.

Bleaching has for its object :

(1) To give the nitrated fibre a greater whiteness, which is important especially for transparent objects, ivories, ambers, &c.

(2) To free the nitrocellulose from the acid which it contains (acidity after nitration in spite of the washings which follow) and also that due to the acid necessary for bleaching.

Every nitrocellulose containing acid, even though this acidity may be always feeble, yields a substance which very quickly decomposes. Hence it follows that there is a very large depreciation of the manufactured material, in addition to the accidents which this decomposition may bring about.

The bleaching of nitrocellulose may be performed by different methods (by means of bleaching powder, free chlorine, potassium permanganate, &c.). The method involving potassium permanganate is the one in general use ; hence we shall only examine this process.

Bleaching by permanganate includes ;

(1) Pulpation of the nitrocellulose.

(2) Treating the cellulose nitrate with a permanganate solution acidified by sulphuric acid of 66° Baumé ;

(3) Removal of the permanganate solution and washing with water ;

(4) Washing with water acidulated by hydrochloric acid ;

(5) Precipitation of the permanganate remaining in the pulp with sulphur dioxide. For generating this gas, sodium bisulphite and hydrochloric acid are employed ;

(6) Sufficient washing to remove every trace of acid from the nitrocellulose.

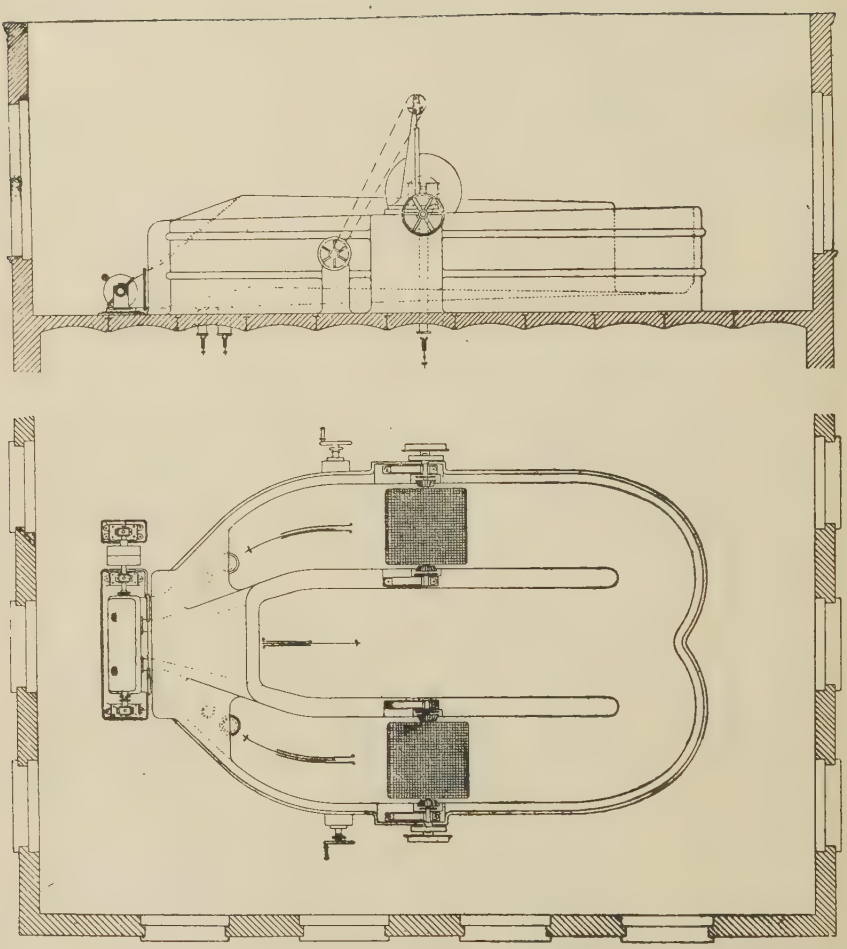
We go on to describe each phase of these operations and the apparatus used in each case.

1. Pulpation of the Nitrocellulose. According to Gerald Sanford we are indebted to Sir Frederick Abel for the idea of making the nitrocellulose into pulp.

The reduction of the nitrated cellulose to the state of pulp is performed by means of a stamp mill (pile), commonly called " the Hollander pile," from the name of its inventor, " Hollander."

Although these machines are also used in paper manufacture we shall give a brief description of them.

PLATE I



VOITH'S BLEACHING PILE

To face page 65

The stamp mill is made up of a vat of ellipsoidal section constructed of stout oak (8 to 10 millimetres thick). This vat, embedded in a block of masonry, is divided into two compartments by a partition, as shown in the appended Figure.

In one of the compartments is a solid cylinder made from a piece of oak upon the circumference of which are steel blades forming teeth, the number of these varying with the diameter of the drum.

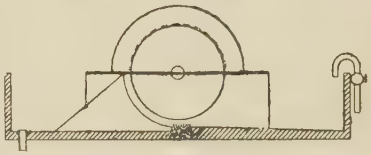


Fig. 27. Hollander pile.

Above this drum is a slab made of a thick oaken plank, carrying steel teeth. This slab is fixed, and by suitable gearing the drum may be made to approach or retreat from the slab at convenience.

Finally, the base of the pile, which is horizontal in the compartment not containing the drum, is raised in the other, and surrounds the circumference of the drum concentrically. The bottom and walls of the pile are usually lined with sheet lead or, better, with copper.

An orifice furnished with a meshed grating, whose meshes are 1 square centimetre in cross-section, allows the pulp to be removed.

In the well-known Horne's pile, constructed by the Voith firm, the slab occupies a very low position, the object being to allow the cylinder blades to work up the paste even when at a very low level. The toothed cylinder is at the extremity of the trough and lifts up the paste from the lowest point of its diameter towards the plate discharging into the open trough, thus providing a large descent for the paste to be triturated.

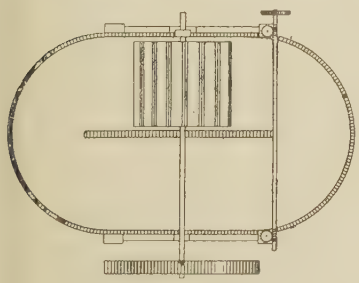


Fig. 28.

The makers have adopted these two arrangements with the object of causing a rapid circulation capable of attaining a speed of 10 to 20 metres per minute, thus rendering stirring unnecessary.

The heavy cylinder is made of iron and furnished with steel or bronze blades having a raising movement.

The piles bring about pulpation in the following way:

After having introduced enough water into the pile to give a sufficiently fluid mass, the nitrated paper is placed in the vat. This paper is carried along by the water current induced by the rotation of the cylinder and just passes between the teeth of the latter and the slab. It is thus torn up.

Paper is continuously fed into the pile, care being taken to keep it in motion, especially at the periphery of the apparatus, where the tendency is for the paper to stop.

The paper constantly passes between the cylinder and slab until, at the end of a certain time variable with the nature of the nitrated cellulose, the regulation

of the pile, &c., when the nitrocellulose has been reduced to a sufficiently fluid paste, it may be sent to the bleaching vat.

The regulation of the cylinder and slab is a delicate matter, since when the space between these two pieces is very small, the pulp is reduced to the state of very fine paste, which appreciably diminishes the yield. Moreover, the overcharging of the cylinder is to be feared. If, on the other hand, the working space is too large, the pulpation is imperfect, thus increasing the working period and prejudicing the efficient emptying of the pile.

What dimensions should a pile possess? Let us consider, for example, the dimensions necessary for a pile capable of making into pulp 300 kilogrammes of nitrocellulose. We may observe here that admitting a yield of about 145 per cent. we must nitrate from 210 to 215 kilogrammes of paper.

At least 20 litres of water should be reckoned per kilogramme of paper unwound.

Further, it is necessary to take into account that 100 kilogrammes of unwound paper require a space of 1 cubic metre after nitration.

We, therefore, have in our example:

(1) *Quantity of water necessary:* 210 kilos × 20 litres = 4200 litres

(2) *Volume necessary for accommodating the paper:*

2·1 k. × 1000 litres = 2100 „

or a total of 6300 „

Our pile must, therefore, contain 6300 litres, and accordingly we shall give it the following dimensions:

Greater axis	4400 mm.
Smaller axis	2500 „
Height	750 „

The cutting cylinder should be 1250 millimetres in diameter, and, like the height, the width of the compartment should be 1250 millimetres.

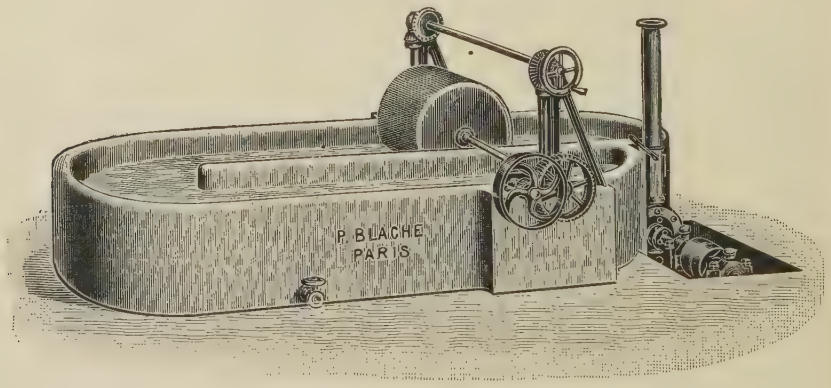


Fig. 29. Bleaching Pile.

This drum should carry on its periphery 30 steel teeth, and should be mounted upon a shaft of 150 millimetres, turning at 120 revolutions per minute.

The slab should carry 18 teeth, fitted into the massive oaken plank, and having a length of 40 millimetres. The width of the slab should be 150 millimetres, and, like the drum, should be 1·25m. in length.

Finally, the walls of the pile as well as the central partition should be 100 millimetres thick.

2. The bleaching proper. We have seen previously that the nitrocellulose, when sufficiently made into pulp, was sent to the bleaching vat, there to undergo the different bleaching operations.

Before detailing the bleaching process, let us examine the construction of a bleaching vat.

The bleaching vat. This is usually a stout truncated or cylindrical vat, of which the diameter is generally double the height. It should be constructed of oak, since this wood best resists the slow but sure destructive action of the acids added during the course of bleaching. The walls of the vat have a thickness of 60 to 80 millimetres, and are securely hooped.

The bottom of the vat is also of oak, and has two or three apertures of 120 millimetres diameter, by which the wash liquors may be drawn off. A valve permits opening or closing. Above the floor of the vat is a false bottom, constituted of thick celluloid plates, perforated by holes 1 millimetre at the most in diameter. These holes are about 1 centimetre apart. This arrangement may be replaced by perforated glazed tiles, such as are usually found in commerce.

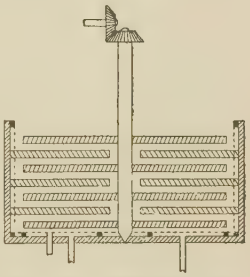


Fig. 30. Bleaching Vat.

To increase the draining facilities, the walls of the vat are sometimes furnished with perforated material or tiles. This system appears to possess many defects, principally those which allow the pulp to become stationary between the vat walls and those of the filter, thereby accelerating the decomposition of this pulp and in consequence soiling the whole mass.

Upon this false bottom is a pipe of 10 to 15 millimetres diameter furnished with a valve. The bleached pulp is withdrawn by this orifice into the draining bath.

At the centre of the bleaching vat is a shaft, pivot mounted, and carrying arms which stir the mass. It is driven by suitable gearing, and makes about 30 revolutions a minute.

The stirring system varies. Sometimes the shaft carries 16 to 20 tiers of arms, as represented in Fig. 30. In the space between the movable arms are fixed ones secured to the vat walls. The mass is thoroughly mixed with this system of agitation.

In a second system, the shaft carries a toothed pinion working on each side two toothed wheels, each of which in turn drives a shaft carrying paddles placed perpendicular to it (Fig. 31).

What dimensions should the bleaching vat possess ? In certain works a quantity of water equal to 25 litres per kilogramme of paper unwound is reckoned for 100 kilogrammes of paper to be nitrated, which should give after nitration from 145 to 150 kilogrammes of nitrocellulose according to the process followed. The fact that 100 kilogrammes of paper after nitration occupy a volume of 1 cubic metre must be taken into account.

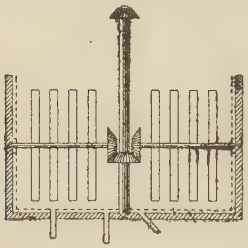


Fig. 31.

It is, therefore, necessary when deciding upon the dimensions to be given to the bleaching vat to allow for 35 cubic decimetres per kilogramme of paper unwound.

We advise, however, this volume to be increased to 40 cubic decimetres, so as to allow for the bleaching agents, which for a perfect bleaching are distributed throughout the entire bulk of the pulp.

If, as in the case of the pile dimensions, we take a quantity of 210 kilogrammes of unwound paper, it is, therefore, necessary to have :

Volume occupied by the pulp : 0·010 mc. × 210 = 2·100 mc.
Volume of water required : 0·030 mc. × 210 = 6·300 „
or a total of 8400 litres.

Moreover, a depth of 100 to 120 millimetres not occupied by the mass should be allowed for.

The following dimensions should, therefore, be given to the bleaching vat :

Diameter	3000 mm.
Depth	1300 „

Let us pass on to the bleaching operations.

1. Treatment with Acidulated Permanganate Solution. The potassium permanganate employed should be as pure as possible. It would, however, be foolish to have recourse to the use of chemically pure permanganate, since the high price of this product would sensibly increase the net cost of bleaching.

What quantity of permanganate should be employed ?

Per kilogramme of paper unwound, 3·5 grs. of potassium permanganate should be added. If the calculation be based on the weight of nitrated paper, 2·3 grs. should be used.

Per hectolitre of water, the quantity of permanganate is 9·23 grs.

This permanganate is first dissolved in hot water (about 15 or 20 litres), and is then filtered so as to hold back all the insoluble impurities which the solution may contain. The latter is then poured upon the pulp contained in the bleaching vat and the stirrers set in motion.

The sulphuric acid is then added. This acid, as previously mentioned should be 66 degrees Baumé.

For the amount of permanganate indicated above, 11 grammes of acid per kilogramme of paper unwound are necessary, or 7·6 grs. per kilogramme of nitrocellulose considered dry.

The acidity of the water therefore corresponds to 0·3 grs. H_2SO_4 per litre.

The sulphuric acid is added in small portions; occasionally it is preferable to add it to a known volume of water, so that the pure acid may not come into direct contact with the nitrocellulose.

What period should be allowed for complete reduction?

The minimum time allowed should be from 2½ to 3 hours. If a better bleaching be desired the time may be extended to 4 or 5 hours. After this interval the water in the vat, which was formerly purple, becomes clear; in contrast the pulp acquires a strong brown colour. In a model works the pulp remains in contact with the potassium permanganate for 12 hours. (500 grammes of permanganate per 100 kilogrammes of paper unwound.)

2. Washing with Water. The action of the potassium permanganate being accomplished, the liquor is run off and replaced by water. The mass is then stirred for about 30 minutes. The object of washing is to remove the oxide of manganese retained in the pulp. After washing, the water is changed and the process renewed.

3. Washing with Acidulated Water. 25 grammes of pure hydrochloric acid of 22 degrees Baumé are poured per kilo. of nitrocellulose pulp, which corresponds to an acidity of 100 grammes per hectolitre of water. Contact, always accompanied by stirring, is allowed for 40 minutes.

In many celluloid works, this washing with acidulated water has been abolished. The washing over, the liquor is replaced by ordinary water.

4. Bleaching of the pulp stained brown by potassium permanganate. This bleaching operation is carried out by gaseous sulphur dioxide, liberated from sodium bisulphite of 35 degrees Baumé by means of pure hydrochloric acid.

For the amount of potassium permanganate indicated above, there are poured into the bleaching vat 30 grammes of sodium bisulphite and 20 grammes of pure hydrochloric acid per 100 kilogrammes of nitrocellulose. This corresponds to a content, per hectolitre of water, of

Sodium bisulphite	115·5 grs.
Pure hydrochloric acid	77 ,,

The duration of contact of the bisulphite with the nitrated pulp is indicated by the disappearance of the brownish colour present. At least two hours are necessary for complete decoloration. If the material stands it, 3 hours contact are allowed, after which the vat liquor is diluted.

At this point the bleaching proper is terminated. It is necessary to

eliminate every trace of acid contained in the pulp, which may be achieved by washing.

5. Washing the pulp. The washings are made with ordinary water. Their number is only limited by the number of bleaching vats in use, and also varies with the works output.

As a general rule, many washings for short periods should be made. In many works, 5 to 6 are made ; in others, the number may extend to 10, the latter figure being preferable.

Washing should always be accompanied by stirring and each one should last 30 minutes.

The acidity of the water in the bleaching vat and that of the pulp must be tested ; the latter is the most sure method of obtaining a good result.

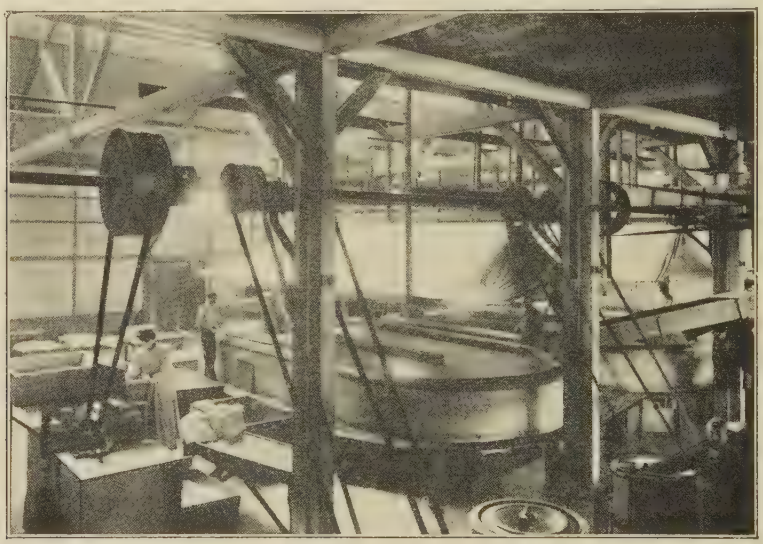


Fig. 32. A Bleaching Chamber.

We recommend a final washing with alkaline water employing per 100 kilogrammes of pulp :

150 grammes carbonate of soda,
100 cubic centimetres of water.

In this way traces of acid which the pulp may retain are certain to be neutralised.

Draining the pulp. When the last washing is terminated, the bleached pulp is sent to the draining vat,

The latter may be any shape but is usually of rectangular section, and is furnished the length of its walls with perforated material allowing the withdrawal of the water which serves as a vehicle for the pulp.

It is necessary to allow a volume of 6·5 cubic metres for accommodating the

amount of nitrated paper which has been taken for the pile and bleaching vat, *i.e.* 300 kilogrammes.

If the section is rectangular the draining vat should have :

Length	6·000 m.
Width	1·200 m.
Depth	0·900 m.

When the water has run off the pulp will only occupy about half this volume.

In this condition the pulp is hydro-extracted.

Hydro-extraction of the pulp. The object of hydro-extraction is to eliminate the water retained by the pulp, although it is impossible to express it entirely.

With a centrifugaliser 1 metre in diameter, making 850 revolutions per minute, it is impossible to remove more than forty per cent. of the water in the moist pulp, *i.e.* 100 kilogrammes of bleached pulp after hydro-extraction should weigh 60 kilogrammes.

By the above apparatus forty-five to fifty kilogrammes are expressed in 30 minutes.

The complete bleaching of the nitrocellulose entails a loss of five to six kilogrammes of nitrocellulose per 100 kilogrammes of paper unwound. Note however that this loss varies between wide limits, according to the mode of working the pile and the kind of apparatus employed.

Bleaching by means of hypochlorite. At the present time bleaching by permanganate has been superseded in many works by bleaching with hypochlorite or hydrogen peroxide. Some firms also use a permanganate washing followed by one with hypochlorite. In reality these two washings are duplicates, and the former may be abandoned without inconvenience. The advantages claimed for permanganate (particularly the oxidation of iron salts) are all possessed by hypochlorite.

Bleaching by hypochlorite has perhaps the inconvenience of requiring a very prolonged washing, not merely with large volumes of water, but by remaining for prolonged periods in water which is renewed several times. The duration of bleaching is increased, and, therefore, the management expenses augmented. What then are the reasons which prompt the selection of this process at the present time?

Free chlorine yields excellent results in the laboratory. Up to now, however, this has not received commercial application.

The Bleaching Plant. We have previously given the dimensions necessary for the pile, bleaching vats and draining baths.

With a pile of the following dimensions :

Larger axis	4400 mm.
Smaller axis	2500 „
Depth	750 „

300 kilogrammes of nitrated pulp may be obtained, and this operation requires a maximum of three hours' work, including the clearance of the pile.

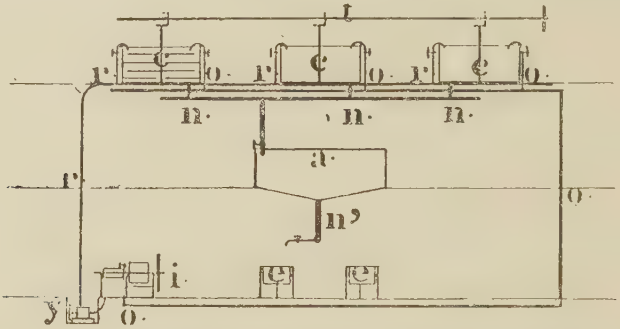


FIG. 33. Scheme of the installation in a Bleaching Chamber.

i. Hollander pile.
y. Centrifugal pump conveying the pulp to the bleaching vats.
r. Pipe system from the pump to the bleaching vats.
c. Bleaching vats. t. Power transmission driving the stirrers
o. Pipe system conveying water to the bleaching vats and pile.
n. Pipe system for running off the pulp water.
a. Tank for receiving the bleached pulp.
n'. Knee pipe feeding the pulp to the hydro-extractors.
e. Hydro-extractors.

This pile will be amply sufficient to convert our 725 kilogrammes of nitrocellulose into pulp.

The vats are according to what we have said above :

Diameter	3000 mm.
Depth	1300 ,,

Each vat has ample capacity for the contents of the pile.

It is necessary to allow for two vats a minimum bleaching period of ten hours. It would be preferable to have three vats installed, so as to be prepared for any extra demand.

There should be two draining baths of the following dimensions :

Length	6000 mm.
Width	1200 ,,
Depth	900 ,,

For the complete hydro-extraction of the pulp two centrifugalisers are necessary, these working continuously for ten hours.

These pieces of apparatus are installed according to very different arrangements.

The most usual disposition consists in placing the pile on the ground level, while a pump sucks the paste from the pile and presses it into vats situated at a higher level. The bleached pulp passes naturally from the vats to the draining tanks. When the bleaching vats are not raised a pump is used to empty them.

CHAPTER VI

THE DRYING OF NITROCELLULOSE

After the nitrocellulose has been bleached and expressed in the hydro-extractor, it is then dried.

The object of drying is to expel the moisture remaining in the pulp after hydro-extraction, *i.e.* about 40 to 50 per cent. of water.

Different systems have been proposed for this purpose, and these we proceed to examine.

The systems are classified in three categories :

(1) Compression and heating.

(2) Compression.

(3) Washing with alcohol.

DRYING BY COMPRESSION AND HEATING.

This process permits of almost perfect drying, and although it necessitates a fairly strong material, it is nevertheless one of the most often employed on account of the excellent results afforded.

We shall deal with each phase of this system, which includes :

(*a*) Division of the pulp.

(*b*) Working into cakes.

(*c*) Compression of the cakes.

Division of the pulp. The pulp proceeding from the centrifugaliser is placed in air-tight cases from which it is taken for division. Let us add in passing, that a capacity of 1·300 mc. per 100 kilogrammes of paper unwound is necessary for lodging the pulp after hydro-extraction.

We have thus :

Paper unwound	100 kil.
Paper nitrated (yield)	145 ,,
Nitrated paper hydro-extracted	250 ,,

Our 25 kilogrammes of hydro-extracted nitrocellulose therefore require 1·300 mc. capacity for storage.

The store case may be of cubical shape and have as dimensions :

Length	1200 mm.
Width	722 ,,
Depth	1500 ,,

This case is made of soft wood lined with sheet zinc.

Let us return to the division of the pulp.

For this purpose mills are used, of which different forms exist, falling into two types:

Cylinder mills.
Ball mills.

Cylinder mills are composed of a shaft, furnished at its lower end with a pulley; above the latter is a circular plate whose upper surface carries a helix.

Above this helix is an independent crown of smaller diameter. This crown is fixed to the upper part of the frame of the mill; the frame is placed in a cylindrical box enclosing the plate carrying the helix, which constitutes the grinder. The lower box of the mill has an orifice which permits the ground pulp to be withdrawn.

The mill works as follows:

When the pulp for grinding is poured into the mill by means of a hopper, it falls into the open space of the crown. The grinder just rubs lightly against the crown and carries away the pulp, which, on account of the rotation of the grinder, passes over the uneven spiral and is then reduced to fine fragments. Centrifugal force projects the pulp against the lower box and thence to the orifice.

To avoid congestion, the shaft of the grinder is mounted so that it can be lowered and so cause the grinder to descend when the mill is overcharged.

This type of mill is mostly employed in Germany and England.

The "*Ball mill*" is similar to those used in other industries, and only differs from them in its more limited dimensions. At present the Cylinder mill, which reduces the pulp to fragments sufficiently small, is more generally employed.

By the aid of these mills 100 kilogrammes of expressed pulp may be ground into very good condition in 35 minutes, using a mill of 500 millimetres diameter making 300 revolutions per minute. Therefore in an hour and a half at the most, 100 kilogrammes of paper unwound, nitrated, bleached and expressed may be fed into the mill.

In every case, the nitrocellulose coming from the mill should be entirely reduced to a fine condition and not contain lumps which would be very difficult to dry.

Working into cakes. In this process the cake is made by hydraulic pressure.

Figure 34 is a representation of the hydraulic press used for forming nitrocellulose cakes.

This press is made up of a plate supported by a plunger allowing the plate to be raised and to press against the top of the press which is fixed. The stroke of the piston is very short, being only 150 millimetres. Upon the plate, which is pierced with holes through which play the press pillars, are two parallel ribs serving to guide the frame in which the cake is formed and which, in short, plays the part of mould.

This frame, made of iron, has usually a square section of 35 by 35 millimetres. It is movable.

Beneath the upper part of the press is provided a square projection 2 centimetres thick and having a section smaller by a few millimetres than that of the frame.

The working of the press will now be comprehended.

The frame supported by a slab of galvanised iron is filled with pulp; this being done the charged frame is placed on the press plate and raised by hydraulic pressure.

The part projecting from the top of the press fits into the frame and the pulp is compressed; on lowering the plate a cake possessing a certain amount of rigidity is produced.

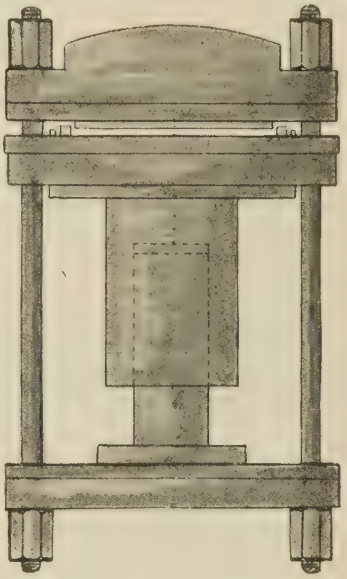


Fig. 34. A Cake-forming Press.

The cake-forming process, although simple, requires minute attention on the part of the operator.

It is necessary that this cake should neither be too thin nor too thick. If the cake is not thick enough it does not adhere and there results much loss at the time of compression. If too thick, it adheres well, but on drying the expulsion of the retained water takes place very slowly and cannot be made complete.

The operator at the press should therefore keep to a suitable average. He should under no circumstances make cakes exceeding 800 grammes with the frame of 500 by 500 millimetres. The limits should be 700 and 760 grammes, a good average being 740 grammes per cake.

The workman should see to the good charging of the frame: for this purpose a shovel of galvanised iron is used. This shovel should serve as a measure, an essential condition in order that the weight indicated above be not exceeded. Especial care should be taken to charge the corners of the frame, these parts being most subject to breakage.

A cotton serviette is placed beneath the frame.

These being done, the operator raises the press by means of the low pressure, *i.e.* 35 to 50 kilogrammes per square centimetre. The frame being in position, the low pressure is cut off and the high pressure substituted (150 kilogrammes per square centimetre).

As soon as the final pressure is attained, the cylinder of the press is emptied, the frame is raised and withdrawn, and it only remains to take the serviette upon which the cake is found. The cakes are left on their serviettes and piled

one upon another. With a press having a square frame of 50 centimetres side, working at 40 kilogrammes low pressure and 150 kilogrammes high pressure, a good workman should make 100 kilogrammes of paper unwound, or 250 kilogrammes of paper nitrated and hydro-extracted, into from 335 to 340 cakes in an hour and a half.

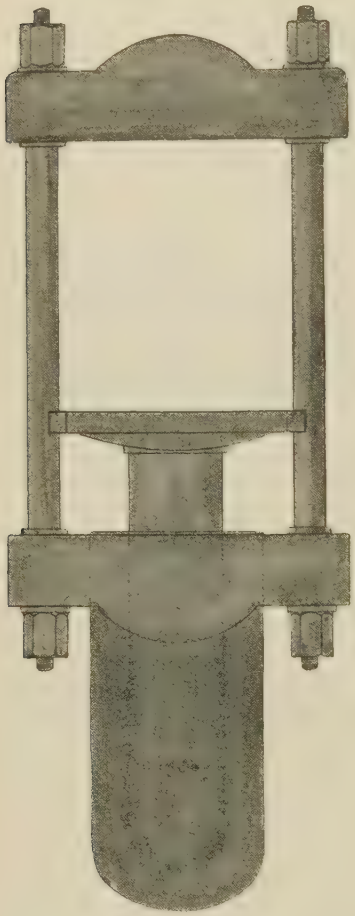


Fig. 35. Press for Drying the Cakes.

We will now pass on to the compression.

Compression of the cakes. This operation includes two successive operations:

Draining.

The compression proper.

Draining. The cakes, proceeding from the press, are laid, separated by their serviettes, under a press which expels their retained water.

These presses are the same as those serving for the compression proper. They are made up of an iron plate supported by a plunger whose cylinder is buried in the ground. The plate is guided by four steel pillars which support the top of the press.

The cakes, piled one upon the other, are placed on the plate of the press. By pressure the plate is raised and finally presses the cakes against the top of the press.

The plate of the press for draining and drying the cakes is generally of rectangular form and measures 700 millimetres long by 600 millimetres wide. The stroke of the plunger has been calculated to allow for the compression of a large number of cakes.

It is usually 750 to 800 millimetres for a plunger length of 1·150 m. to 1·250 m.

This press, like that employed for making cakes, may work at low or high pressure.

To be carried out properly, draining requires a period which varies a little with the quantity of cakes pressed. In general the more cakes pressed the longer the compression period, since the cakes felt and tend more and more to retain their water. The best method would be to work with repeated compressions. As the average time of drainage compression for 150 to 170 cakes an hour should be allowed.

This draining only brings about a loss of 12 to 13 per cent. of the weight of water retained in the hydro-extracted pulp.

Therefore, 170 cakes drained for an hour, the average weight of a cake being 740 grammes, or a total weight of 125·800 kil. have, after draining, a weight of 109·500 kil., or 110·700 kil.

The compression proper. The cakes being relieved of the greater part of the water which may be extracted from them by the press, are placed in heated serviettes and subjected to renewed compression.

The cakes, after draining, are removed from the wet cloths, these being replaced by serviettes taken from a drying chamber.

This change having been performed, the pile of cakes is replaced under the press; the high pressure is turned on and after a given interval relieved, this process being continued until the cake retains no further moisture.

The duration of the compression proper varies with the warmth and thickness of the cloths.

Usually cloth serviettes are used, which for square cakes of 50 centimetres side are 1200 millimetres long by 600 millimetres wide.

The cake is placed at one side of the cloth, which is folded so as to cover the cake completely; this is done for each in turn.

We always recommend the employment of very thick cloths, which retain their heat best and cool least during the transit from the drying chamber to the presses.

With plain serviettes 12 to 15 compressions are necessary, the drying chamber being heated from 35 to 38 degrees Centigrade.

The duration of each compression should be about 10 minutes, and the average time required for two assistants to arrange the cloths at each pressing is 7 to 8 minutes.

The serviettes employed immediately after the draining operation are wet, and therefore require a lengthy stay in the drying chamber; in consequence it is well always to utilise these for packing the cakes as they emerge from the draining press.

The drying chambers are often divided into two categories; the first containing the hot cloths, the second those less warm.

These two groups of drying chambers are heated to the same temperature, but the second, containing the moister cloths, furnish those less warm.

We recommend the following routine for drying the cake:

(1) Draining.

(2) Compression of the cake wrapped in the less warm cloths.

(3) Compression in the hot serviettes.

We have previously mentioned that 12 to 15 compressions are necessary for drying the cake completely; from the fifth the hot serviettes should be used.

More than 170 cakes per press should not be taken, *i.e.* about the yield from 50 kilogrammes of unwound paper or 125 kilogrammes of expressed pulp.

The following is the result of a complete drying trial carried out upon 171 cakes obtained from 150 kilogrammes of expressed pulp.

Operations	Time of commencement	End	Duration	Time for serviette adjustment	Observations
	hrs. min.	hrs. min.	min.	min.	
Draining	6 10	7 10	60	11	Temperature of the drying chamber containing the less warm cloths, 33° C.
Compression					
1st	7 21	7 30	9	12	
2nd	7 42	7 52	10	10	
3rd	8 2	8 13	11	11	Temperature of the drying chamber containing the hot cloths, 35½° C.
4th	8 24	8 34	10	11	
5th	8 45	8 57	12	12	
6th	9 9	9 19	10	11	After the 4th compression hot cloths are employed.
7th	9 30	9 42	12	10	
8th	9 52	10 2	10	13	
9th	10 15	10 26	11	10	
10th	10 36	10 48	12	11	
11th	10 59	10 9	10	12	
12th	11 21	11 31	10	10	
13th	11 41	11 52	11	11	
14th	12 3	12 14	11	10	
15th	12 24	12 35	11	—	
Duration of the compression			3h. 40m.	2h. 45m.	Total drying period, 6h. 25m.
Time for cloth adjustment .			—	—	

According to the preceding Table it follows that 15 compressions must be made before obtaining a pulp which does not include more than $2\frac{1}{2}$ to 3 per cent. of moisture.

Everything depends on the temperature to which the drying chambers are heated, and also, as already mentioned, on the thickness of the cloths. It is obvious that when the surrounding temperature is cold, the cloths will become cold less readily if they are very hot.

The two following trials show the part played by the heating of the wrappers. These trials were carried out in a cold climate and in the middle of a winter which was very severe. Three cakes of different weights were taken and submitted to identical temperature conditions.

The comparison of the two following trials is significant:

In the first trial, where the cloths were only slightly heated, 15 compressions were necessary for obtaining a cake which still held 3·15 per cent. water. In the second trial, where the drying chambers were hotter, 1·41 per cent. moisture was found by analysis after 13 compressions.

If thick cloths are used the drying is readily accomplished by 10 compressions.

The following conclusions may be drawn:

(1) A drying chamber heated at 38 to 40° must be used for less warm cloths.

(2) A drying chamber heated at 48 to 50° for hot cloths.

(3) Cloths must be employed formed by the juxtaposition of 6 simple serviettes.

The Drying Chambers. The serviette-drying chambers are heated by steam. They are usually built of masonry.

Numerous drying systems are in existence.

In the first place we will describe the following arrangement.

Trial No. 1

Operations	Weight of the cake at each compression			Loss suffered at each compression			Observations
	A 724 gr.	B 690 gr.	C 661 gr.	A 724 gr.	B 690 gr.	C 661 gr.	
	gr.	gr.	gr.	gr.	gr.	gr.	
Draining	697	665	621	27	25	40	Temperature of the drying chamber for the less warm serviettes, 32° C.
Compression							
1st	665	642	609	32	23	12	
2nd	640	618	589	25	24	20	
3rd	613	587	559	27	31	30	Temperature of the drying chamber for the hot serviettes, 38° C.
4th	592	566	537	21	21	22	
5th	575	550	520	17	16	17	
6th	553	534	497	22	26	23	Duration of compression, 5h. 50m.
7th	544	529	487	9	14	10	
8th	531	511	481	13	18	6	
9th	521	502	472	10	9	9	Hydraulic pressure, 150 kil. per sq. cm.
10th	511	490	467	10	12	5	
11th	505	487	460	6	3	7	
12th	501	481	459	4	6	1	After the 5th compression the hot serviettes were used.
13th	492	473	453	9	8	6	
14th	492	471	449	0	2	4	
15th	486	467	447	2	1	2	

Trial No. 2

Operations	Weight of the cake at each compression			Loss suffered at each compression			Observations
	A 724 gr.	B 690 gr.	C 661 gr.	A 724 gr.	B 690 gr.	C 661 gr.	
	gr.	gr.	gr.	gr.	gr.	gr.	
Draining	699	664	622	25	26	39	Temperature of the drying chamber for the less warm serviettes, 32° C.
Compression							
1st	663	640	601	36	24	21	
2nd	635	611	582	28	29	19	
3rd	605	583	553	30	28	29	Temperature of the drying chamber for the hot serviettes, 38° C.
4th	584	564	535	21	19	18	
5th	570	550	512	14	14	23	
6th	551	532	493	19	18	19	Duration of compression, 5h. 50m.
7th	539	517	478	12	15	15	
8th	514	501	463	25	15	15	Hydraulic pressure, 150 kil. per sq. cm.
9th	502	487	555	12	14	8	
10th	484	476	444	18	11	11	
11th	480	468	441	4	8	3	After the 5th compression the hot serviettes were used.
12th	479	465	440	1	3	1	

The drying chambers are built of bricks and placed one after the other as shown in the following Figure.

In the diagrams we have two drying chambers, A B.

The posterior part of the dryer is occupied throughout its whole length by a

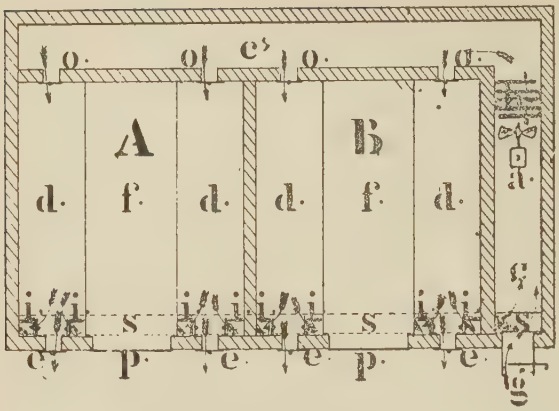


Fig. 36. Drying Chamber (plan).

chamber carrying the steam pipes. In the partition separating this hot chamber from the drying chambers are apertures through which the hot air penetrates.

These openings *o* are furnished with valves capable of regulation.

The hot air after its stay in the drying chamber escapes through holes to the regulated openings *i*, which communicate with apertures by which it escapes into the atmosphere. By suitably adjusting the outlet valves a hot air circulation is induced.

It is preferable to place a fan in the hot chamber whereby a rapid circulation of hot air is brought about.

In this case, as shown in the Figure, there exists a pipe *s* (*see* Fig. 36), which returns a portion of the hot air to the fan and thus diminishes steam consumption.

The drying chamber plant includes a central service passage *f*, on whose sides are cupboards *d*, closed by frames working in a groove and secured by catches.

In these cupboards the cloths are suspended from rails.

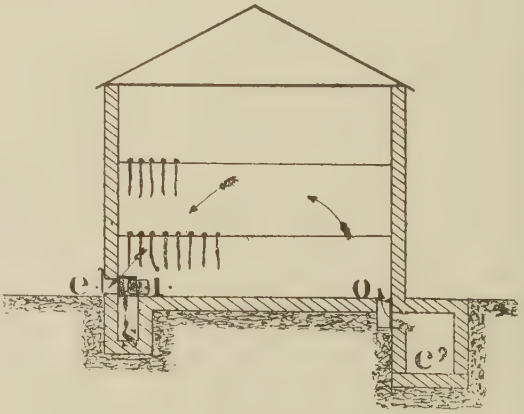


Fig. 37. Drying Chamber (section).

a and c. Steam pipes. d. Drying section.
e. Valve for regulating the air inlet.
i. Valve for regulating the hot air exit.
b. Service passage.

In another drying system the circulation is brought about by a draught chimney.

Each drying chamber is separate and the heating is performed by steam pipes which circulate all round the chamber in trenches, above which are provided flues whose draught can be regulated by means of a valve. A circulation of hot air thus results which, beginning at the bottom, traverses the cloths and then escapes into the atmosphere.

The steam pipes on the ground level require to be carefully covered with masonry. This precaution is indispensable, otherwise the particles of nitrocellulose which always adhere to the cloths would fall on the hot pipes and

inflame with great ease. Similarly the pipes passing beneath the central chamber should be well insulated, otherwise there would be a danger of conflagration.

In the case of many drying chambers the escape steam pipe from one passes to the other chambers.

Dimensions of the drying chambers. These chambers should be built twenty-two centimetres thick, *i.e.* double-bricked walls. The service passage is 1200 millimetres above the ground level, and the heating trench is 800 millimetres above the soil; there exists, therefore, 400 millimetres under the service passage.

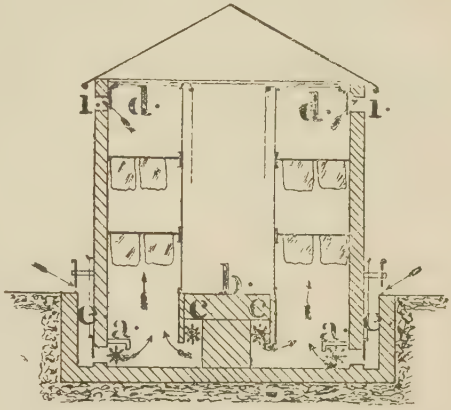


FIG. 38.- Drying Chamber.

The rails are placed 1 metre above the service chamber, *i.e.* 2·200 m. from the bottom of the heating trench. A second row of rails may be placed 1·200 m. above the first.

The length of the drying chamber, calculated approximately for drying the cloths necessary for 340 cakes produced from 100 kilos. of unwound paper, allowing one serviette per cake, should therefore accommodate 340 serviettes. It is necessary, however, in order to give the requisite interval for drying the cloths, to employ, when working continuously, treble this accommodation, *i.e.* 1020 serviettes.

Now, when calculating upon only one row of cloths drying, this number should be halved, since there are two compartments, *i.e.* 510 cloths per compartment. A space of 8 centimetres must be allowed in the direction of the breadth of the rail.

The drying chamber should, therefore, be at least 4 metres; 4·500 m. will give all the space necessary.

The recess of the cupboards should be 1200 millimetres, and the width of the service passage 1600 millimetres. The drying chamber should, therefore, have a width of: 2 (1200) + 1600 = 4000 millimetres.

The height of the chamber,

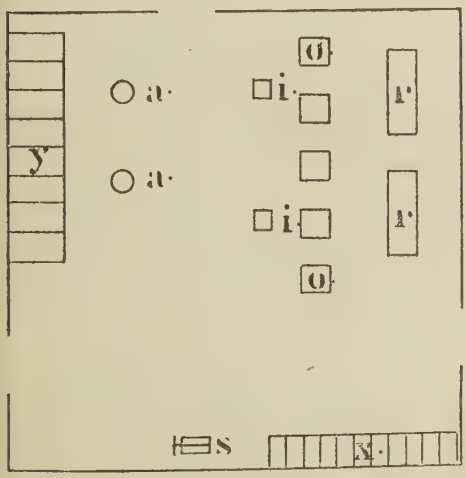


FIG. 39. Scheme of the Installation of a Cake Drying Plant.

y. Cases of moist pulp.
a. Pulp mills. i. Cake presses.
o. Cake drying press.
v. Work tables.
x. Cases of dry pulp.
s. Cake grinder.

according to what precedes, should be at least 3500 millimetres above the ground level.

In each compartment there are four walls.

The steam should arrive at the drying chambers under a pressure of 4 kilogrammes, and in winter it should be maintained as far as possible at about 5 kilogrammes.

In many works wood is employed for the walls, this being the most convenient material in spite of its great combustibility. Iron has the inconvenience of retaining the heat it incidentally receives and so occasioning frequent accidents.

The construction of reinforced cement affords the greatest security, although the alternations of moisture and dryness naturally accelerate its deterioration.

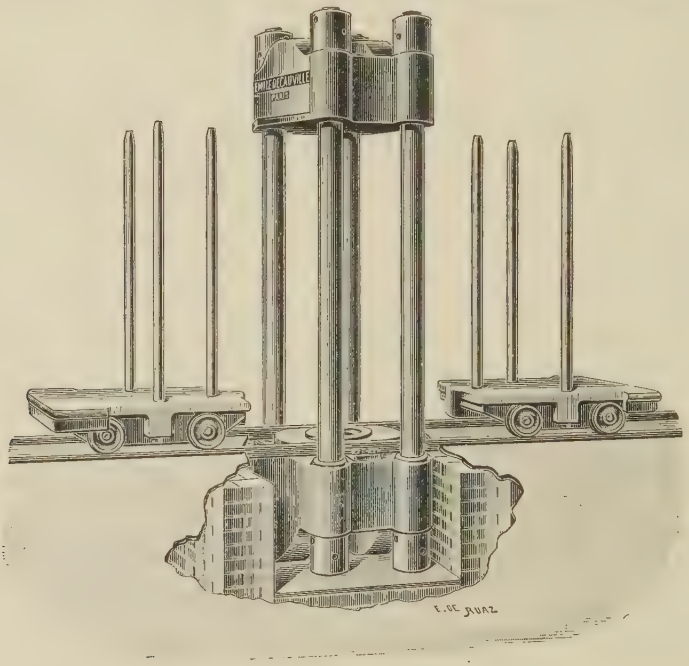


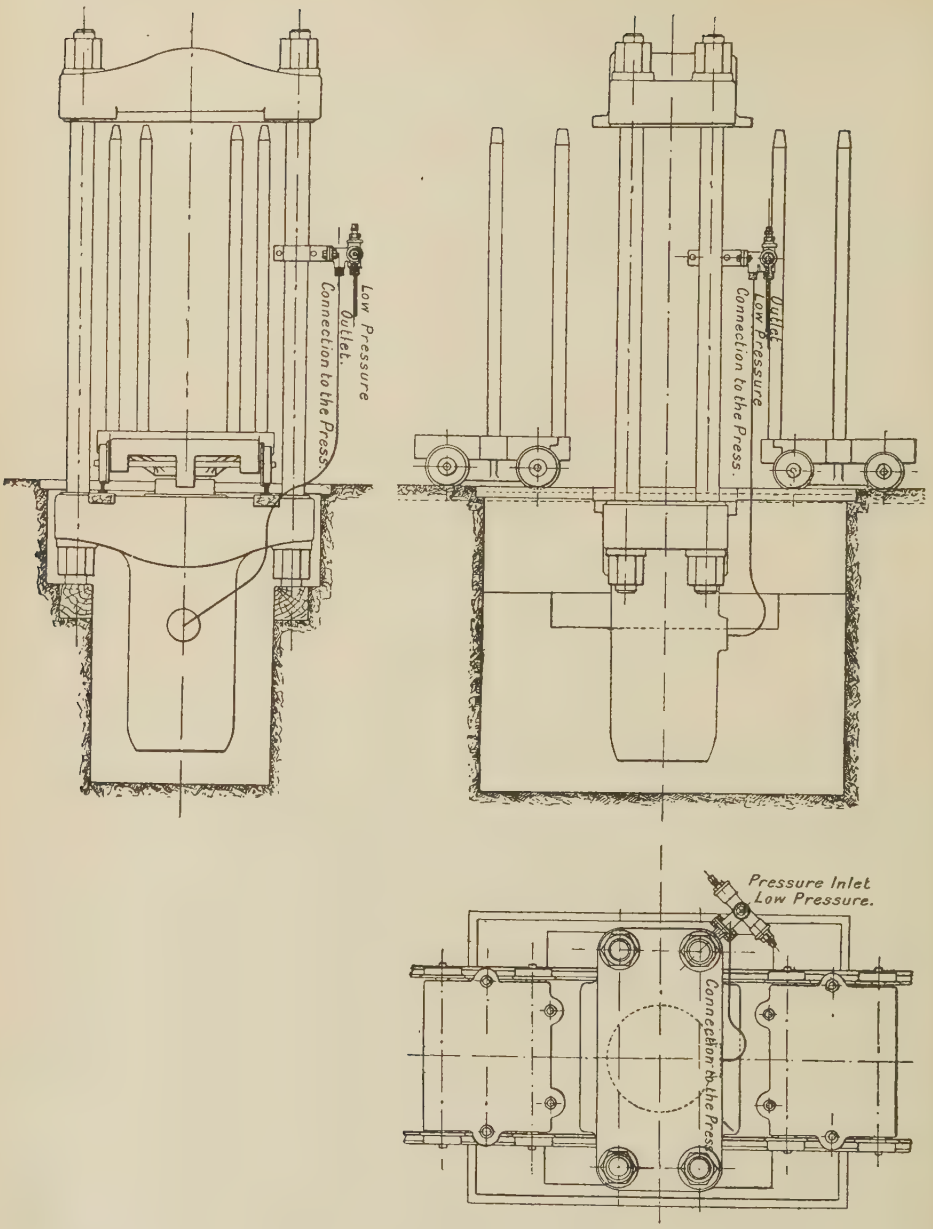
Fig. 40. Cake Drying Press.

The essential point is that the places on which the particles may fall should not be too hot.

In a drying chamber heated to about 50° C. an hour and a half is necessary to dry the serviettes used for wrapping up the cakes which are not moist.

In the dryer where the less warm cloths are placed, two hours must be allowed. The drying period depends on the valves for admitting air and on the exit of the hot air.

PLATE II



CHAMPIGNEUL'S CAKE-DRYING PRESS

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Drying by Compression.

The tendency is more and more to abolish drying by compression and heating, and to substitute a simple compression of the cake.

For this purpose truck presses are employed, which are constituted similarly to the drying press already described, but are unprovided with a plate and carry a truck mounted on rails, which may be placed when desired upon the plunger of the press. When the pile of cakes becomes dry, the press is lowered and the truck run away, being replaced by another.

Very few of the older firms employ the system of press drying in which the hot wrappers are abolished and the drying brought about by simple compression. Fig. 40 represents one of these presses having a capacity of 100,000 kilogrammes constructed by the Decauville firm, which with the firms of Morane and Champigneul make, in France, a speciality of all material for celluloid manufacture.

Drying by Means of Alcohol.

The moist pulp is placed in a centrifugaliser containing alcohol. The alcohol absorbs the water in the pulp.

The latter, diluted, is recovered and restored to its original condition by distillation.

The alcohol drying process practised in Germany is much more scientific than the original and expensive method of press drying. Infinitely better economical results are obtained. Unfortunately it is difficult to apply in France, the excise being an almost insurmountable obstacle. Press drying is in consequence the sole method employed.

According to Böckmann, drying by means of alcohol was formerly performed in Richard France's apparatus, which combined pressure with alcohol washing.

The firm of Selwig and Lange construct a turbine specially designed to displace the water contained in the nitrocellulose by alcohol without compression, and at the same time to alcoholise the nitrocellulose. The cage possesses, outside the external wall, a metallic case perforated internally and a circular lid of aluminium or bronze covering the space between the two walls. In the annular space thus formed and lined with sackcloth is packed the moist nitrocellulose; then the special circular lid is fixed and also the hinged cover of the turbine.

After starting the turbine, a known amount of dilute alcohol, which has been already used, is introduced by an injection pipe traversing the cover and pierced with holes at the extremity; this is completed by the addition of alcohol of convenient strength.

The turbine is allowed to work for a known time.

The nitrocellulose proceeding from the turbine contains from 30 to 33 per cent. of alcohol. The capacity of the cage is 60 kilogrammes, and the yield from the turbine in 10 hours is about 600 kilogrammes.

In Germany many of these turbines are in actual use in celluloid works.

Installation of the nitrocellulose drying plant.

The nitrocellulose drying plant should include:

(1) Cupboards for the expressed nitrocellulose;
(2) Stands for the mills;
(3) Boxes for storing the ground nitrocellulose pulp;
(4) Stands for the cake presses;
(5) Cake tables;
(6) Drying presses;
(7) Tables for manipulating the cakes;
(8) Cases for the dry cakes;
(9) The cake grinder.

Finally, outside the drying workshop, or the portion of the building where this work is carried out, are the drying chambers. We shall give the space occupied by each apparatus in the case of a separated plant, supposing that the works unwinds 500 kilogrammes of paper per day of 10 hours.

With 145 per cent. yield we have 725 kilogrammes of nitrocellulose which give, after bleaching and hydro-extraction, 1232 kilogrammes of moist pulp.

(1) *Storage of the pulp.* We have seen that 1·300 mc. are necessary for storing 250 kilogrammes of expressed pulp. Therefore 5 pulp cupboards are required of dimensions:

Length	1200 mm.
Depth	722 „
Height	1500 „

These 5 cases are placed along one of the workshop walls, which should therefore have a length of 6 to 7 metres.

(2) *Pulp mills.* An hour and a half is necessary for grinding up 100 kilogrammes of expressed pulp; therefore half the weight produced by the nitration of 500 kilogrammes of paper may be ground per day.

Two mills should be installed occupying a space of 10 square metres when they are driven from below.

For ball mills the space will only be 8 square metres. The space required for two boxes, in which the ground pulp is received and the pulp for grinding contained, should also be reckoned.

(3) *The cake press.* The cake press occupies a maximum space of 1 square metre.

The box containing the pulp to be made into cakes takes up 2·500 square metres. As for the cake table, it should be 2 metres long by 800 millimetres wide per cake press. A single press should suffice for making the 1232 kilogrammes of expressed pulp into cakes. The production may be extended to 1500 kilogrammes.

(4) *The cake drying press.* We have seen that 125 kilogrammes of expressed pulp may be dried in 6 hours. Therefore for drying 1232 kilo-

grammes of pulp 5 presses are necessary. Each press occupies a space of 1 square metre.

(5) *The wrapper tables.* Two tables are necessary: they should possess the following dimensions:

Length	3500 mm.
Width	1000 „
Height	800 „

These tables should stand on a platform raised 150 mm. above the ground and projecting 1 metre on each side of the width of the table.

Fig. 41. Workshop for Drying Nitrocellulose Cakes.

The wooden, well-polished floor, should be 5·700 m. long by 3 metres broad. It serves to collect the pulp which falls during the wrapper manipulations.

(6) *Cupboards for the dry cakes.* The cupboards are formed of cases closed by means of sliding doors and placed 700 mm. from the ground.

These cases, destined to receive 145 kilogrammes of dry pulp, have as dimensions:

Length	600 mm.
Depth	1100 „
Height	600 „

In them two piles of dry cakes are placed. The storage of two days' output should be reckoned; *i.e.* 10 cases placed in line and occupying a space 7 metres in length by 1·500 m. in width.

(7) *The drying chambers.* Two dryers of the type described last suffice

for ensuring the output of the serviettes necessary for the cake produced. One serves for heating the less warm serviettes, the other for the hot ones.

Upon the scheme showing the position occupied by each apparatus a large space is left over; it is in these spaces that the steeping of the waste is performed. We shall return to this later.

The staff necessary for the drying operation is:

At the mill			2 men.
„ „ cake press			1 man.
„ „ drying press	Presses		2 men.
	Manipulation of the wrappers and cakes		8 assistants.
„ „ drying chambers			2 men.

CHAPTER VII

STEEPING THE NITROCELLULOSE

GRINDING THE CAKE.

The cake could hardly be employed in the condition it arrives from the drying press. Before steeping it is ground into small parts, which thus dissolve more readily in the camphorated alcohol employed in the steeping process.

For this purpose a grinding machine is used which usually consists of two cylinders, *a* and *b*, 10 centimetres in diameter, carrying cylindrical teeth and placed in such a way that during rotation the teeth of one cylinder fit into the spaces of the other.

Two toothed pinions, geared one into the other and driven by a pulley, cause the cylinders to revolve in opposite directions. The grinder is generally made of bronze.

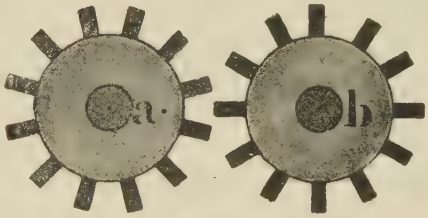


Fig. 42. Cake Grinder (section).

To grind the thin cakes, two or three sheets are taken and after being folded they are passed between the cylinders, whose teeth penetrate and reduce them to fragments of size varying with the space between each tooth. A box placed beneath the apparatus receives the ground pulp. These fragments should be at the most 4 square centimetres. The grinder is mounted upon two cast iron feet and occupies a maximum space of 1 square metre.

A good workman may pass through the grinder under good conditions 300 kilogrammes of cakes per hour.

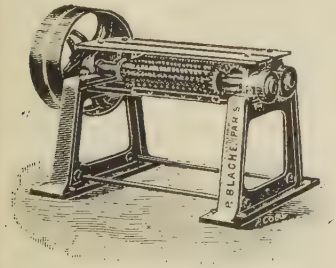


Fig. 43.

THE STEEPING PROPER.

By "steeping" we mean the operation whereby nitrocellulose is mixed with alcohol and camphor to form a paste which, when rolled and pressed, gives celluloid.

Böckmann, in his treatise on celluloid, describes in the process of Hyatt Bros., of New York, the transformation into paste in the following manner: "The pyroxylin, pressed and dried, is crushed, sifted and mixed with camphor. In other cases the guncotton, washed and dried, is ground with Hollands.

After sufficient pulverisation the Hollands is run away, and the mass subjected to strong pressure in a perforated vessel. The spirits are expelled and a fairly hard and sufficiently moist body is obtained; to avert all danger of inflammability the product is mixed with camphor under water."

The above description of the process is inaccurate. Camphor is never mixed with pressed and dried pyroxylin, but only with pyroxylin which has been merely expressed. The washed and bleached nitrocellulose pulp is expressed, and on emerging from the centrifugaliser, while containing about 40 per cent. water, is mixed with camphor.

The following is how Hyatt Bros. proceeded, and also how the American celluloid manufacturers still act.

The mixture of expressed nitrocellulose and pulverised camphor is made in special mills whose grinding discs are horizontal and whose axes are not in the same straight line. In America this grinder is known under the name of the "Bogardus Mill."

The mixture proceeding from these mills is formed into thin cakes, then compressed in the hydraulic press at about 150 kilogrammes per square centimetre between cloths or sheets of blotting-paper until dry. This compression is repeated a certain number of times until the water content has attained an amount which varies with the works.

When this content is not more than 10 to 12 per cent., it is rolled in a rolling mill heated to about 65° C., in this way the nitrocellulose and camphor are intimately mixed and the solution of the pulp assured. This process requires a lengthy stay in the rolling mill to evaporate all the water which the pulp contains.

It may happen that the material possesses badly adhering parts, which may deteriorate the celluloid manufactured from it; often also the latter is milky, especially for light tints, and a lengthy stay in the drying chamber is necessary for this slight opacity, which gives a bad effect, to disappear.

In many works the cakes after press drying are subjected in dryers, formed of chambers or closed apparatus, to the action of a current of dry air which is slightly heated, or are placed in vacuum drying chambers. The water content may thus be reduced to about 3 per cent.

This process has the objection of promoting a small loss of camphor by evaporation in the drying apparatus.

In Europe no celluloid firm employs the American method.

According to M. Séguin[1] the Stains Company work as follows: the nitrocellulose containing 40 per cent. water after hydro-extraction, is mixed with camphor in the proportion of 30 camphor to 100 nitrocellulose, to which are added colours insoluble in water. The mixture is brought about between two horizontal grindstones sliding one over the other. The mixture being imperfect, it is submitted to compression for moulding into cakes about 2 centimetres

[1] *Bulletin de l'Inspection du travail*, 1904 (numbers 3 and 4). Note on Celluloid Manufacture, by M. Séguin, Department Inspector of Works at Paris.

thick, which are wrapped in cloth and subjected anew to a compression of 150 kilogrammes per square centimetre. This operation is thrice repeated, the cloths being changed each time.

This treatment is then followed by one with alcohol. M. Séguin adds: "The mixture is still not intimate enough; it is an imperfect celluloid. By means of a lens particles of camphor and nitrocellulose may be discerned in it. Treatment with alcohol is therefore carried out."

The cakes are crushed and soaked in cold alcohol in the proportion of 30 alcohol to 100 of the camphor-nitrocellulose mixture.

Aniline colours soluble in water and alcohol may be added, since these are not lost by the evaporation of the solvents in the drying chambers.

The nitrocellulose-camphor-alcohol mixture is then formed into cakes, which are taken to a rolling mill heated at 60° C.

Certain firms, as we have seen, replace press drying by a 90 per cent. alcoholic lixiviation, which at this strength has hardly any solvent action on nitrocellulose.

The content of water and alcohol depends on the mixing and hydro-extraction. In Selwig and Lange's turbine, as we have mentioned in the preceding chapter (*see* Drying by Alcohol), the final alcoholic content is from 30 to 33 per cent.

The steeping may next be carried out by the addition of alcohol (96 degrees) and camphor in the normal proportion of 100 nitrocellulose, 40 camphor, and 80 alcohol.

The method at present preferred in Europe to the American process consists in drying the nitrocellulose as completely as possible, either by alcohol or by the cake drying press, as mentioned in the previous chapter, before making the admixture with camphor.

The steeping is made by mixing the nitrocellulose pulp which has been washed, bleached in the bleaching vat or, better, in the bleaching pile, expressed and dried, with solvent formed of camphorated alcohol.

THE PRACTICE OF STEEPING.

This operation may be carried out in two ways:

(1) Manually, by means of steeping boxes.

(2) Mechanically, by employing kneaders.

Steeping in boxes. By means of a large spatula the ground nitrocellulose is mixed in a suitable box with the solvent. The whole is covered by a lid to avoid evaporation of the solvent, by whose contact the nitrocellulose gelatinises.

The duration of steeping varies with the composition of the mixture. The boxes employed should be very strong and especially watertight. The bottom, in particular, should be very durable, since to remove the dissolved nitrocellulose tongs are used which may rapidly deteriorate it.

Certain firms employ wooden boxes lined with sheet zinc. Others prefer boxes constructed entirely of galvanised sheet iron.

The latter, although heavier, last longer than wooden boxes and appear preferable to us.

In practice the steeping of 100 kilogrammes of nitrocellulose necessitates a capacity of 300 cubic centimetres.

The box should possess the following dimensions :

Length	1000 mm.
Width	750 „
Height	400 „

It is well to have inclined sides, which facilitate the manipulations necessary for emptying the box.

The box is constructed of galvanised sheet iron, 10 to 18 millimetres thick, the edges and base being strengthened by corner irons.

The duration of steeping when carried out in a box by means of the following normal composition :

Nitrocellulose	100 kgr.
Camphor	40 „
Denatured alcohol	80 litres

is from 8 to 10 hours.

These are normal figures, but very often the rolling is not made until after 12 and 15 hours contact.

These figures hardly differ for other steeping mixtures. The quality of the nitrocellulose is especially influenced by the duration of steeping. In all cases the tendency is to substitute mechanical kneaders or mixers for box steeping.

Kneaders. These machines present the following advantages over steeping boxes :

(1) Diminution of the steeping boxes, which occupy considerable space.
(2) Decrease in the time necessary for dissolving the nitrocellulose.
(3) Diminution in the quantity of solvent necessary for solution.

We have seen that 10 hours (the normal period) are necessary for steeping 100 kilogrammes of nitrocellulose.

With the kneader 1½ hours at the most are required.

Again, an average of 120 litres of camphorated alcohol per 100 kilogrammes nitrocellulose must be taken for box steeping.

With the kneader, the solution of nitrocellulose requires a maximum of 100 litres camphorated alcohol.

These advantages largely compensate for the purchase price of the machine by the economy effected.

It has been stated that the kneader gives a yellowish colour to the nitrocellulose through the action of the hot alcohol ; but this slight coloration, which only affects the nitrocellulose employed in the manufacture of transparent

materials and of certain ivory tints, may be corrected by the use of suitable colours.

In principle, the kneaders are composed of a receiver of rectangular section, whose base is constituted of two parts of circular section, thus forming two basins having a cylindrical surface.

Above these two basins are two shafts upon which are fastened arms whose two branches are opposite.

The shafts are driven by two toothed wheels which are revolved by two pulleys turning in opposite directions and at different speeds.

By a special arrangement, the apparatus may be worked in either direction at will, or even mechanically reversed in order to extract the dissolved pulp.

A cover, provided with a safety valve in case of over-pressure, prevents alcohol evaporating from the kneader.

Finally, the kneader is jacketed so that the interior of the kneader may be heated, this being brought about by a circulation of hot water whose temperature should not exceed 70° C. Usually the temperature is 60° C.

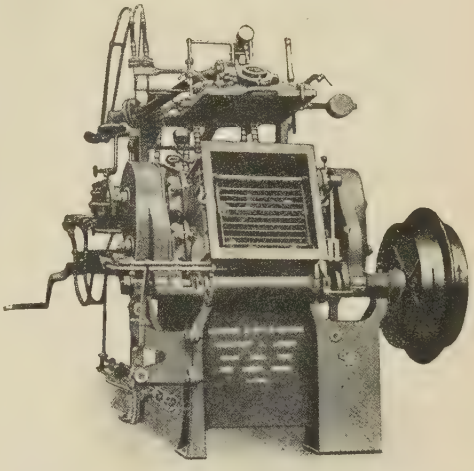


FIG. 44. Mechanical Kneader of the type "Celluloid Vacuum" with an arrangement for working in vacuo.

To obtain efficient working the capacity of a kneader taking 100 kilogrammes of nitrocellulose should be 300 litres; the amount of nitrocellulose kneaded is thus augmented.

Working at an average of 65° C. with the steeping indicated above, and employing the usual nitration formula, 100 kilogrammes of nitrocellulose may be kneaded in $1\frac{1}{4}$ hours.

The total duration of the operation is $1\frac{1}{2}$ hours.

A kneader of this size has therefere ample accommodation for treating the 720 kilogrammes of nitrocellulose produced by the kind of installation we have selected as an example.

With the object of diminishing the net cost of celluloid, the loss of alcohol vapour when emptying the kneader must be reduced to a minimum. To avoid too great a loss by evaporation the celluloid manufacturers only add the amount of alcohol actually necessary for bringing about solution. This precaution increases the working period, since the gelatinisation of the nitrocellulose takes place more rapidly when in presence of a large quantity of solvent. With an excess of alcohol a quicker and much more complete gelatinisation is brought about.

The use of a vacuum kneader eliminates loss when working up the pulp in presence of excess, and allows the recovery of the alcohol by means of the vacuum, which is usually at about 700 mm.

Figure 44 represents a type of mechanical kneader, "The Celluloid Vacuum," constructed by the firm of Werner-Pfleiderer, and complying well with the conditions desired.

It is composed of a vat mounted on a strong cast-iron frame, upon which are fixed the various accessories of the machine. The vat, of cast iron, is jacketed at the curved base so as to permit of heating by the circulation of steam or hot water.

Steel paddles are carried by axles maintained in bearings supported upon side cheeks. Stuffing boxes secure a perfect tightness to any passage from these cheeks, and avoid the introduction of oil or grease by suction into the material undergoing treatment.

The paddles are driven at each extremity by suitable gearing. The vat is furnished with a cast-iron lid of pyramidal form, possessing two apertures for observing the work, and fixed to the vat by tight joints.

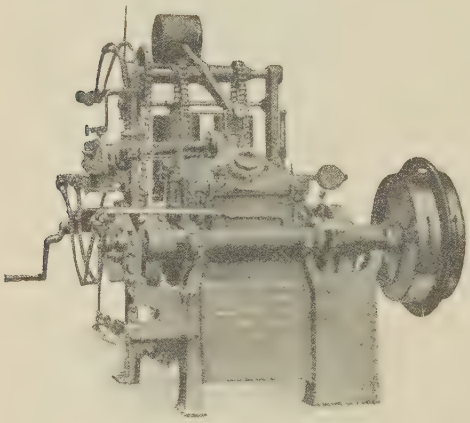


Fig. 45. Kneader Mixer of Werner-Pfleiderer with the cover raised and the vat reversed.

The raising of the lid is performed by a counterpoise or by a chain gear and counterpoise. This lid possesses a thermometer for ascertaining the internal temperature of the vat, a manometer, and a valve for connecting with the vacuum pump.

A vacuum of 700 to 720 mm. may be maintained in the apparatus when working.

The machine is furnished with a reversing arrangement, whereby a forward or backward motion of the paddles may be obtained at convenience without any other intermediate throwing out of gear.

For discharging, the vat may be reversed by means of a hand winch and balanced counterpoise. The lid may be heated or not, and must be provided with a safety appliance combined with the disengaging lever, so that the workman may avoid introducing his hands into the apparatus when working. The latter precaution is demanded in certain countries by the laws governing works accidents.

Figures 46 and 47 represent a small experimental plant, consisting of a Universal type of Vacuum Kneader Mixer of 18 litres capacity, with vacuum pump and recovery apparatus.

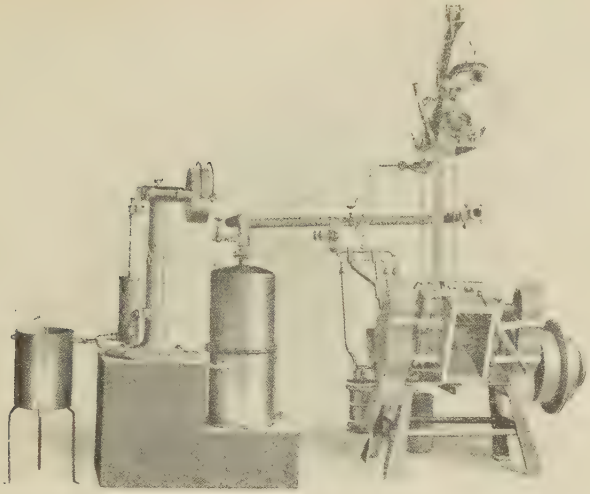


FIG. 46. Kneader Mixer with Vacuum Pump and Recovery Apparatus (apparatus open).

The capacity of such an apparatus may vary from 80 to 100 litres; the most usual dimensions employed are from 200 to 400 litres. With vacuo kneaders a very complete gelatinisation of the pulp is obtained, which appreciably

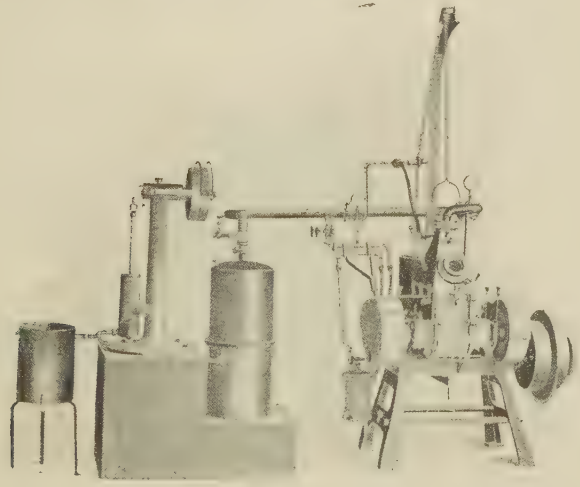


FIG. 47. Kneader Mixer with Vacuum Pump and Recovery Apparatus (apparatus closed).

diminishes the work of the rolling machine. Now, this point is very important, because during the latter operation a very pronounced evaporation is produced on account of the cylinder temperatures.

We cannot however entirely dispense with the rolling machine, since the

material should be made into sheets in order to be compressed under good conditions. But this work is reduced to a minimum, and moreover the pulp does not undergo rolling until after the excess of alcohol has been evaporated and recovered.

Preparation of the Camphorated Alcohol. The camphorated alcohol is prepared in the following way. Into a bath of dimensions varying according to the amount of mixture required is first poured the denatured alcohol, and then the camphor, which has been broken into small fragments for quicker solution, is dissolved in it. To diminish the solution period, a portion of the alcohol may be heated and poured while hot upon the mass of camphor; this heating process, however, causes the alcohol to evaporate, and occasions loss. It is best to place the receiver, which is made of galvanised sheet iron, in a heated chamber whose temperature should be 25° C. in winter and 20° C. in summer.

What should be the content of the mixture in camphor and alcohol?

The proportions of camphor and alcohol in the mixture are extremely variable. Böckmann adds to the pyroxylin half its weight of solvent containing one part of camphor for eight of alcohol. The solution of the pulp is only brought about at an elevated temperature.

The majority of authors recommend the mixture of two parts nitrocellulose for one of camphor. As a general rule, the more camphor present the better the quality of the celluloid manufactured. The maximum should be from 45 to 50 per cent. of camphor. It is extremely unusual, however, that the industry employs such quantities of camphor, because of its high price. When the price of camphor is low, advantage is taken to increase the amount employed. A good alcoholic mixture should contain, per cent., from 40 to 45 kilos. of camphor and from 60 to 55 litres of alcohol. In order to transform 100 kilogrammes of camphor into celluloid, 96 to 100 litres of the camphor-alcohol mixture should be employed—the latter in the proportion of 58 to 60 litres of alcohol per 42 to 40 kilogrammes of camphor. After rolling, 170 to 180 kilogrammes of soft celluloid are obtained.

Every firm endeavours to decrease these amounts, but we believe it impossible to lower these figures without risk of miscalculation.

The alcohol employed, whatever its mode of production, should be perfectly colourless, should register 94° to 96° on the alcoholometer, and above all possess no trace of acidity. The alcohol is denatured before use; for this purpose methylation is generally adopted. The use of coloured methylated spirits, which, in spite of the small quantity used for denaturing (10 to 12 per cent.) give yellow mixtures of camphorated alcohol, should be avoided. In Germany, celluloid firms are authorised to denature alcohol by dissolving 1 per cent. of camphor in it. The same tolerance is desirable in France, substitutes for ethyl alcohol have been proposed, such as, methyl alcohol, acetone and ether, but the high price of these products prohibits their use. Toluene alone may perhaps be of advantage.

The camphor employed varies with the quality of the product to be manufactured. Three different qualities of camphor are on the market—white camphor, grey camphor, both from Japan; and China camphor.

The two former are generally suitable, the white camphor not being coloured like the second and only possessing traces of oils. The grey camphor on analysis often gives 1 to 4 per cent. of oil according to the samples, to which moisture is often added. Finally China camphor, of soiled and oily appearance, contains more of the lighter solid impurities, from 8 to 10 per cent., and occasionally more oily and greasy materials.

In America, where the powdered camphor is mixed with the expressed nitrocellulose, it is indispensable to have a pure and suitable camphor; the celluloid manufacturers, however, have almost in all cases a plant for purifying or refining camphor.

White camphor is employed exclusively for the manufacture of transparent celluloid and ivories. Grey camphor is reserved for the manufacture of other articles. As for China camphor, it is only employed for second-rate articles. In many works, grey and China camphors are mixed, for the manufacture of tortoise shells, simple colours, &c., to obtain a steeping solution which is not too yellow. The net cost of manufactured celluloid may thus be diminished.

We give, in the sequel, some formulæ for steeping the nitrocellulose produced according to our recipe, suitable for use in the manufacture of different materials.

Let us declare at the outset that to obtain 100 kilogrammes of well-dried material for delivery, it is necessary to steep 85 kilogrammes of nitrocellulose. This figure may be diminished, but it is necessary to allow for loss of matter undergone during the cutting process. We shall return to these subjects at a suitable place.

Materials	Nitrocellulose	Camphors			Denatured alcohol	Toluene	Acetone	Observations
		Grey	White	China				
	kilog.	kilog.	kilog.	kilog.	litres	litres	litres	
Shells, sheets and rods	85	35	—	—	48	—	2	Good material.
	85	14	20	—	46	—	5	Shell of best quality.
	85	24	—	11	50	—	—	Second rate.
	85	33	—	—	36	16	—	„ „
Ambers and amber coloured horns	85	13	—	—	53	—	—	
	85	13	21	—	51	—	—	Good quality.
	85	17	16	—	52	—	—	„ „
Ivories . .	110	—	50	—	80	—	—	Box steeping.
—	110	—	46	—	78	—	—	Kneading.
White . .	85	—	45	—	37	—	—	
Transparent .	90	—	55	—	45	—	—	Box steeping.
—	90	—	54	—	40	—	—	Kneading.

We shall therefore perform our steepings upon 85 kilogrammes of material. This weight must be increased when we manufacture veined materials requiring several manipulations.

As we have mentioned the steeping formulæ may have very different compositions.

To many of these works' solvents, especially in Germany, castor oil is added, which dissolves perfectly in the alcohol, and whose function is to render the material supple. Usually from 10 to 30 grammes of oil per kilogramme of nitrocellulose steeped are taken.

We recommend 15 grammes should castor oil be added, which will be 1275 grammes per normal block. As a general rule, however, this addition is not to be recommended since it gives a soft celluloid even when present in small proportions. It is only in certain cases, *e.g.* in the manufacture of white celluloid for American cloth, or again for cinematograph films, that this addition serves any purpose. On the other hand, for celluloid designed for the comb industry castor oil must be absolutely prohibited.

Camphor substitutes. We shall see in the third part of this volume that camphor is frequently replaced, whole or part, by certain substances possessing similar properties.

We will only mention here that the most common industrially are: acetanilide, mannol, celludol, and metacelludol. (See Part III. Camphor Substitutes).

The proportion of these elements in the mixture should always be limited, and a product is seldom obtained possessing all the properties and characteristics of a celluloid manufactured with 45 per cent. camphor and 60 per cent. alcohol.

OTHER PROCESSES.

We have just described in detail the principal industrial processes for the manufacture of celluloid. We shall only briefly mention some other processes which may hardly be dismissed without comment in a comprehensive book, but which do not appear to have received extended commercial application.

The object of many of the following processes is to purify the nitrocellulose and obtain a celluloid free from foreign matter.

Chardonnet's process. The cellulose to be nitrated is laid in running acid at 150 to 170° C., into which the foreign incorporated matters fall. After nitration a product is obtained which dissolves in the usual solvents.

Morane's process. The object of this patented process is to obtain a nitrocellulose free from impurities.

The nitrocellulose not containing more than 15 to 20 per cent. water, after being made into cakes, is dissolved in a readily volatile solvent and the solution forced through a purifying apparatus by which the impurities are retained; then it passes into a closed chamber, connected on one side with an exhauster and on the other with a channel containing steam pipes. The temperature of the chamber air should be near the boiling-point of the solvent. The ventilator forces the vapours and aspirated air through a cooled condensation apparatus.

The solution of purified nitrocellulose passes by the main pipe into a series

of small, very fine, additional pipes, through which it emerges into the hot air as very fine threads ; the heat causes the solvent to evaporate and the threads pass almost dry into a basin situated on the floor of the chamber.

The mass of these threads may then be mixed with camphorated alcohol, kneaded and rolled. Preliminary solution should, according to the author, facilitate rolling, and by this process a very pure celluloid should be obtained as well as the solvent recovered by condensation.

Magnus's Process. Nitrocellulose contains 25 per cent. of water. 50 parts by weight are dissolved in 100 parts of ether. Also 28 parts by weight of camphor are dissolved in 5 parts of alcohol ; each solution is made up in pots closed by a caoutchouc plate. The two solutions are mixed, and a plastic mass obtained, which may be readily rolled and which hardens as the ether evaporates. This process is very dangerous.

THE STEEPING OF THE WASTE.

We shall in a later chapter discuss the utilisation of the waste, and the important part it plays in the industry.

Moreover, in this chapter, we shall point out how the waste may be steeped in order to be worked up and transformed into celluloid. The amount of alcohol and camphor necessary for softening the waste and bringing it into a condition for rolling, varies with the state of hardness and the kind of steeping employed. In general, only very little time is reserved for working up the waste, and that accruing when block celluloid is cut up, which has not been in the sheet drying chambers, retains its softness for a considerable time.

Before steeping the wastes, they are crushed in the rolling mill.

We shall examine the crushing process in the chapter dealing with rolling.

Box steeping is still carried out in many works. These boxes are similar to those employed for steeping nitrocellulose. It is well to have them of larger dimensions.

For example :

Length	1250 mm.
Width	900 ,,
Height	500 ,,

Up to 150 kilogrammes of waste may readily be steeped in these boxes.

The tendency, however, is more and more to supplant the slow box steeping by the use of mixers in which the waste is worked up with hot alcohol.

The duration of box steeping is extremely variable.

It is necessary, nevertheless, to allow a minimum period of from 15 to 16 hours. Taking into account works exigencies, this period may be extended without inconvenience to 24 hours.

For the normal steeping of 100 kilogrammes of waste it is necessary to allow:

5 kil. of camphor,
20 litres of denatured alcohol.

There are no absolute rules for steeping; the workman knows by experience how to increase the quantity of camphorated alcohol according to the greater or less dryness of the waste.

We shall see, when dealing with waste utilisation, what plant is necessary for steeping the waste produced by a works unwinding 500 kilogrammes of paper per day.

CHAPTER VIII

THE STAINING OF CELLULOID

Celluloid is stained with great ease, and, moreover, when the operation has been well carried out, the colours are fast for relatively a long time. Prolonged exposure to sunlight alone decolorises the stained material fairly rapidly.

The beauty of the tints depends principally on the state of bleach of the nitrocellulose employed. The latter depends not only on the bleaching, but also on the cellulose used, and on the purity of the waters employed for washing after the bleaching operation. This last point is very important.

Two varieties of colours are used for staining celluloid, viz., mineral and organic.

Mineral colours. Mineral colours are used for producing either semi-opaque materials or those entirely so.

Of mineral colours the most common are:

Brilliant yellow, Naples yellow, cadmium yellows, zinc white, cobalt blue, Cassel earth, natural black ochre, natural raw sienna, burnt sienna, English green, Verona green, cinnabar, some blacks, and many others.

Further, mixtures of these colours are employed. The following compositions, for example, give good mixtures:

1.	Carmine red	10	grammes
	Common zinc oxide	190	„
2.	Ultramarine	60	„
	Common zinc oxide	40	„
3.	Ultramarine	60	„
	Common zinc oxide	43	„
4.	Pale vermilion	5	„
	Common zinc oxide	45	„
5.	Pale vermilion	6	„
	Madder lake	1	„
	Common zinc oxide	43	„

The majority of these colours are insoluble in alcohol, and are employed in the form of impalpable powders, which are slightly moistened with alcohol and directly incorporated with the material during rolling.

Organic colours. The organic colours employed for the staining of celluloid are legion.

Almost all are soluble in alcohol, and are usually made up into alcoholic solutions of required strengths. These solutions or their mixtures are then employed.

Among dyes of organic origin the most common are:

The chrysoïdines R E E, J E 4, brown IV., catechu brown, Lyons blue, light blue, Max's blue, buttercup yellow, golden yellow, ruby, red, rose, orange, brilliant green, crystal green, &c. &c.

It is best to prepare solutions containing 10, 20, 30, 50, and 100 grammes of dye per litre of alcohol either denatured or camphorated. The solution must be filtered.

The following are examples of typical organic colour recipes:

Dyes	Compositions				
Denomination	Colour		Alcohol denatured by methylation	Camphorated alcohol	Distilled water
	Nature	Quantity	Quantity	Quantity	Quantity
		grs.	cc.	cc.	cc.
Chrysoïdine No. 1	Chrysoïdine JEE	100	1000	1000	—
,, ,, 2	,, 59 ST	70	1000	1000	—
,, ,, 3	,, REE	120	800	1000	200
Golden yellow	Golden yellow O	50	1000	1000	—
,, ,, No. 1	Auramine yellow O	30	1000	1000	—
,, ,, ,, 2	Buttercup yellow	40	800	1000	200
Orange ,, 1	Orange J 2893	80	800	1000	200
,, ,, 2	,, 2851	30	800	600	600
Red ,, 1	Fuschin	400	1800	—	200
,, ,, 2	Ruby	40	1600	—	400
Rose ,, 1	Rose P 1920	40	1000	1000	—
,, ,, 2	Rose Bengal	60	950	950	100
,, ,, 3	Cyanosine O	80	900	1000	100
Blue ,, 1	Light blue	100	1000	1000	—
,, ,, 1	Royal blue	40	1000	1000	—
,, ,, 3	Lyon's blue	8	1600	—	400
,, ,, 4	Glacier blue	60	1600	—	400
Violet	Violet B	200	1800	—	200
Green No. 1	Brilliant green	1000	10,000	—	—
,, ,, 2	Crystal green	120	2000	—	—
Ordinary brown	Brown IV.	100	1000	1000	—
Catechu brown	Catechu brown	80	2000	1000	—
Brown No. 1	Bismarck brown	100	950	1500	100
Typical Colour Mixtures					
Orange No. 3	Chrysoïdine REE	80	1250	1500	250
	Orange 1851	30			
	Brown IV.	12			
Orange No. 4	Chrysoïdine REE	40	1300	1500	200
	Orange 2851	10			
Yellow No. 4	Solution orange No. 3 =				80 cc.
	,, golden yellow =				200 cc.

COLOUR TRIALS.

The trial block having been prepared, the rolling takes place with the addition upon the roller of the colour mixture believed to be necessary for obtaining the shade desired. The mixture is poured in small portions by means of a test-tube, so that the final result is not affected by any loss of colour. From time to time a test piece is cut off for comparison with the pattern. The whole operation constitutes a delicate series of tests for which a great amount of practice is necessary. In every case the shade should always appear a little deeper on the roller; after drying the shade becomes lighter.

Colours in powder form, afrer being moistened with alcohol, are placed in contact with the material in small quantities by means of a spatula.

SOME COLOUR RECIPES.

For some types of commercial celluloid the corresponding colour recipes have been established.

The amounts of colour necessary are in inverse ratio to the thickness of the material. For opaque substances the quantities are the same as for the thick ones.

Materials laid on.

Ordinary white. For 100 kilogrammes of nitrocellulose are added:

Mineral white	500	grammes
Light zinc white	2500	,,
Light blue	1·25	,,
Violet	1	,,

To the whole mixture is added one-tenth of camphorated alcohol to prevent loss of colour powder.

Ivory No. 1. For 100 kilogrammes of nitrocellulose:

Mineral white	1852	grammes
Light zinc white	4571	,,
Pale vermilion	1·19	,,
Madder lake	0·25	,,

Ivory No. 2. For 100 kilogrammes of nitrocellulose:

Mineral white	1600	grammes
Light zinc white	4213	,,
Madder lake	0·18	,,
Pale vermilion	0·98	,,

Ordinary black. For 100 kilogrammes of nitrocellulose:

Ultramarine	1425	grammes
Lampblack	419	,,
Alcohol black	76	,,
Light blue	400	,,
Crystal green	6·15	,,

Flower rose. For 100 kilogrammes of nitrocellulose :

Mineral white	1380	grammes
Zinc white	3425	,,
Rose bengal	310	,,

Colours not laid on.

Slightly dark tortoise shell. For 100 kilogrammes of nitrocellulose :

Brown part	100	kilogrammes
Transparent part	120	,,

Thicknesses to be cut from 18 to 22 tenths.

Violet	25	grammes
Brown IV.	45	,,
Nacarat (light red)	210	,,
Chrysoïdine	167	,,
Light blue	9·5	,,
Compact bitumen	320	,,

The latter is dissolved in a small quantity of hot toluene. The other colours are dissolved in camphorated alcohol. About 3 litres of alcohol are required for this preparation.

Light tortoise shell. For 100 kilogrammes of nitrocellulose :

Brown part	100	kilogrammes
Transparent part	120	,,

Thicknesses to be cut from 18 to 22 tenths.

Brown IV.	69	grammes
Ponceau	100	,,
Chrysoïdine REE	95	,,
Light blue	5	,,
Bitumen	270	gr. dissolved in toluene

Solution in 5 litres of camphorated alcohol.

Tortoise shell for rods. (Diameter from 28 to 32 tenths of a millimetre.) For 100 kilogrammes of nitrocellulose :

Brown part	100	kilogrammes
Transparent part	135	,,
Light blue	5	grammes
Chrysoïdine	127	,,
Brown	67	,,
Compact bitumen	100	,,

In all these tortoise shells the proportion of brown to that of transparent varies with the diameter of the rods and the thickness of the material. The greater the thickness, the more the parts of transparent-material and the less of brown.

Amber No. 1. (Thickness from 28 to 22 tenths.) For 100 kilogrammes of nitrocellulose:

Kaolin	185 grammes
Chrysoïdine REE	2 ,,
Brown IV.	0·5 ,,
Light zinc white	105 ,,
Orange 2850	1·5 ,,
Golden yellow	21·5 ,,

Amber No. 2. (Thickness from 24 to 26 tenths.) For 100 kilogrammes of nitrocellulose:

Light zinc white	43 grammes
Cadmium yellow	30 ,,
Golden ,,	15·5 ,,
Indian ,,	38·5 ,,
Orange J	3·2 ,,

Amber horn. For 100 kilogrammes of nitrocellulose:

Mineral white	420 grammes
Light zinc white	140 ,,
Ultramarine	11·3 ,,
Cobalt blue	26 ,,

Cut in thicknesses from 19 to 21 tenths of a millimetre.

Ordinary transparent. For 100 kilogrammes of nitrocellulose:

To be cut into 5 tenths.

Ultramarine	13·5 grammes
Light blue	7·22 ,,
Cobalt blue	6·8 ,,

For thicknesses of 10 to 12 tenths.

Ultramarine	9·25 ,,
Light blue	4·10 ,,

Transparent for accumulators. For 100 kilogrammes of nitrocellulose:

Violet	1·63 grammes
Max's blue	0·92 ,,
Cobalt ,,	8·31 ,,

To be cut in thicknesses of 18 to 22 tenths.

CHAPTER IX

ROLLING. COMPRESSION

ROLLING.

The object of rolling is to terminate the solution of the nitrocellulose commenced during steeping, and also to mix all the parts of material thoroughly together so as to produce perfect homogeneity and a uniform distribution of the colours.

These results are obtained by using the rolling mill.

ROLLING MILLS.

Description of the machine. The rolling mill consists of two horizontal cylinders, one of which is carried by a fixed axle, while the axle of the other may be caused to retire from or approach the former by means of two screws working two slide-blocks in which pass the extensions of the shaft of the movable cylinder.

The cylinders are supported by a strong iron frame, and carry at their left extremity two toothed wheels which revolve the cylinders at the same speed in reverse directions. At the right hand side of the frame is a harness of gearing, which transmits the driving movement.

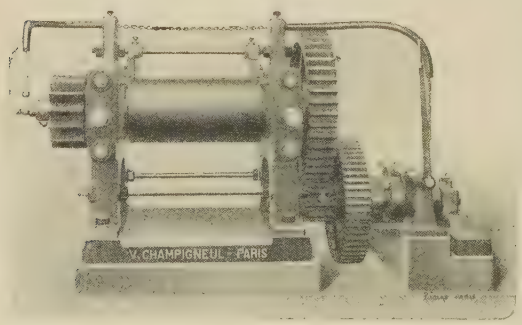


Fig. 48. Champigneul's Rolling Machine.

A hand, and sometimes an automatic disengaging gear, permits the machine to be instantly stopped.

At the extremity of the driving toothed wheel are two tubes passing into the interior of the hollow cylinders, and mounted in such a way that steam or cold water may be sent at convenience into the interior of the cylinders so as to heat or cool them respectively.

The rolling machines are made in two designs, viz., those for average work, whose cylinders are 300 millimetres in diameter, and machines of large capacity having a diameter of 500 and even 650 millimetres, such as the rolling mill in the above figure made by the firm of Champigneul of Paris. The length of the cylinder in both these designs is 1 metre. Under the cylinders is a box into which fall the particles of material and the alcohol.

The use of the large sized rolling mills is more advantageous on account of the increased output they afford, this only requiring about 10-horse power.

The cylinders of the rolling mill should rotate at a speed varying from 12 to 15 revolutions per minute according to the diameter. They should be constructed of tempered cast iron, cast in metal moulds, and absolutely unscratchable with a knife. They are provided with two iron or hard wood guards placed at the ends and destined to prevent the material projecting from either side of the cylinders.

THE ROLLING PROCESS.

The rolling of simple materials. When the nitrocellulose is dissolved sufficiently, the rolling is performed. This operation is one of the most delicate in the manufacture and requires great experience.

As a preliminary the rolling machine must be heated. The degree of heating is variable with the material to be rolled, and constitutes an operation demanding great skill from the operator. The temperature of the rolling mill should be maintained at about 60° C. We recommend not to exceed 65°. The temperature 60° is quite sufficient to terminate the solution of the nitrocellulose.

The rolling operations comprise two distinct phases:

(1) *The drying* of the material, with the object of expelling the alcohol and other solvents retained by it.

It is during the drying operation that the staining of the celluloid is brought about.

(2) *The rolling proper*, which completes the preceding operation and assures the homogeneity of the mixture of material and colour.

During drying, both cylinders should be absolutely heated to the same temperature. Should the rear cylinder be hotter than the fore, the material would leave the latter and adhere to the former.

On the other hand, during the rolling proper, the front cylinder is always hotter than the one behind.

When the temperature is at the correct point, the nitrocellulose, which forms a compact mass in the steeping box, is cut up by knives. Blocks of material (9 to 10) are thus obtained, which are placed upon the roller so as to form round the cylinder a thickness of 13 to 16 millimetres of material. The roller is allowed to rotate for about 20 minutes, during which the necessary colours are added, while for thorough mixing the strips retained between the cylinders are cut with a knife; a greater homogeneity is thus obtained. After the period indicated, the material is withdrawn and a fresh block placed on the roller. The sheet taken away is placed upon a table situated by the side of the operator. The latter cuts up the sheet into rectangular strips (8 to 10 strips).

Each block of steeped nitrocellulose is rolled in the manner just indicated and 10 to 12 heaps of strips are obtained, each heap including 9 to 10 strips.

The drying lasts about $3\frac{1}{2}$ hours.

The rolling proper is then carried out.

A parcel of strips, obtained by cutting sheets withdrawn after the drying operation, is taken and placed upon the roller. An absolutely certain mixture is thus brought about. The strips upon the roller are frequently cut and, after rolling period of about 10 minutes per packet, the sheet is withdrawn. The atter, contrary to that which happened during the preliminary rolling, should e perfectly smooth and possess dimensions slightly less than those of the press.

To execute this operation properly, the material is cut parallel to the cylinders, then, taking the extremity of the cut sheet by the left hand it is drawn away while allowed to rest upon the cylinder which tends to remount it. It is supported by means of the right hand. Next placing the sheet upon the table, it is pressed uniformly upon the cylinder for 5 to 6 millimetres and then passed over it after being folded in four.

A sheet is thus obtained with no wrinkles and having greater dimensions than those of the block press. It only remains to cut away the surplus material. Some minutes should be allowed for the skrinkage of the material to terminate.

By operating in the manner just described, 16 to 20 kilogrammes of material are rolled at each operation, and therefore about $5\frac{1}{2}$ to 6 hours are required with a single roller for rolling 85 kilogrammes of nitrocellulose steeped under the conditions previously indicated. From 140 to 150 kilogrammes of pressed material are obtained.

In certain firms where the operations of nitration, bleaching, and cake drying are not made under good standard conditions, two rollings must be made. The first is imperfect and only lasts from 4 to $4\frac{1}{2}$ hours. The material is pressed, cut, freed from impurities, steeped afresh and submitted to a second rolling. The drawback to such a practice is obvious, and naturally this method of working tends to disappear.

Usually two machines are employed for rolling plain materials, which divide the work of drying and rolling.

In general, one may calculate that an operator can work up from 35 to 38 kilogrammes of material per hour.

The rolling of complex materials. Among the latter tortoise shells mostly predominate.

Tortoise shell is composed of brown and transparent materials mixed in various proportions according to the design.

We shall give the general method of procedure for obtaining tortoise shell. The brown and transparent materials are first rolled apart and at the same time. The period of the rolling-drying process is extended a little, while the rolling proper is very short. When they are sufficiently hard, the brown and transparent sheets are withdrawn and cut by means of a knife into squares having a side of 7 to 8 centimetres. These squares are mixed and taken to the rolling proper.

For the latter, a space of 7 to 8 millimetres is left between the cylinders and

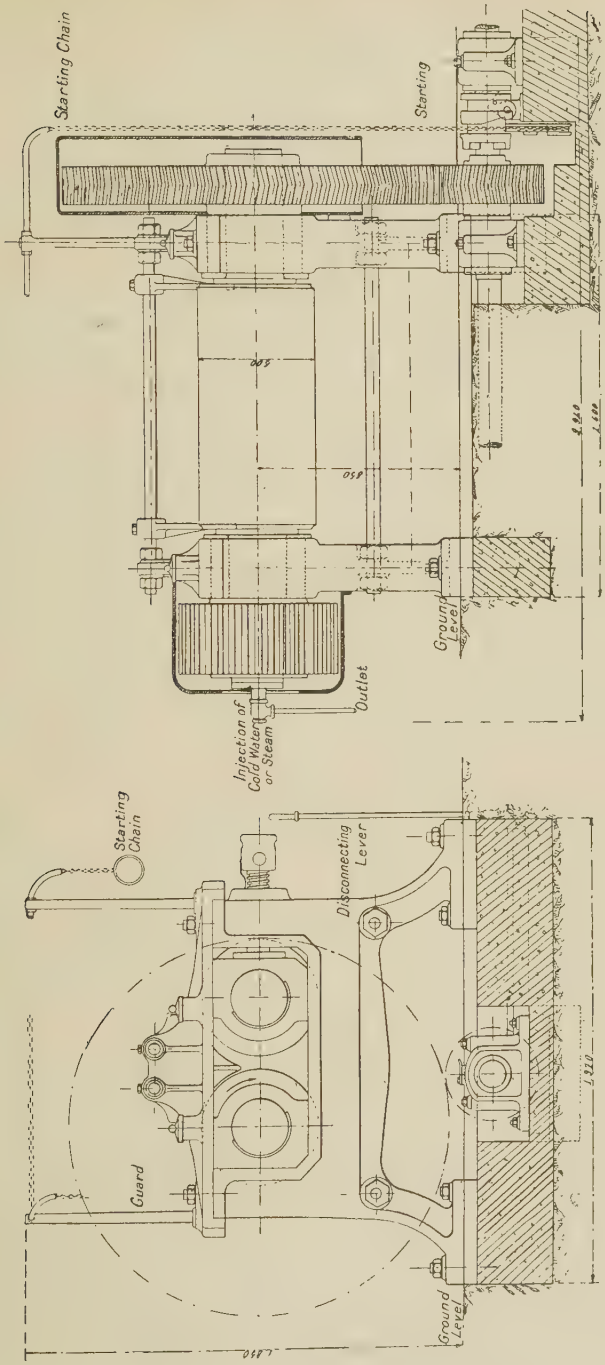


FIG. 49. Decauville's Rolling Mill. 1000 × 500.

the mixture of squares quickly placed in it. They are then crushed, and so mixed together. Some minutes are allowed in the rolling mill so that the colours may be well ground, and then the sheet is withdrawn.

The duration of rolling upon which the mixing depends varies according to the design to be obtained; in certain of these latter, small cubes of transparent material are incorporated during the mixing, giving the transparent specks encountered in certain shells, notably in the shell known as 425 *bis*.

The withdrawn sheet is either cut into fragments, or into strips, which are even knotted in some designs.

The quantity of brown and transparent material may be divided into 4 parts, containing 18 to 20 kilogrammes per part. As far as possible the work is carried out with 4 rolling mills, two for drying the transparent and the other two for drying the brown materials. Afterwards the design is made upon a single roller, which is a little warmer for this effect.

A shell may be completely rolled, starting out with 85 kilogrammes of nitrocellulose or 140 to 150 kilogrammes of material, in $2\frac{1}{2}$ to 3 hours.

The difficulty for the operator is to give the same degree of hardness to the dark and transparent materials. This result is very difficult to obtain, especially when using waste which enters largely into the making of shell.

The rolling of the waste. The rolling of the waste is made in the same way as that of new material. Nevertheless the cylinders should be longer heated, because the waste is dissolved much less readily than nitrocellulose. One is often obliged to divide the rolling into two operations. The object of the first is to transform the mass into sheets, which are steeped anew. After a certain interval the material is again rolled, and is then found to be well dissolved and homogeneous.

When a second rolling is necessary, there are added per 100 kilogrammes of waste:

From 3 to 4 kilogrammes of grey or China camphor, and from 20 to 24 litres of denatured alcohol.

One to two hours are necessary for dissolving the portions of undissolved waste. With one rolling mill, 5 to $5\frac{1}{2}$ hours are necessary for rolling 100 kilogrammes of waste.

We have said, in regard to waste steeping, that the waste is crushed before steeping. An ordinary rolling mill, usually detached, serves for this purpose. The cylinders of the rolling mill are more or less near together, according to the thickness of the waste material, and the latter is thrown in small portions between the cylinders, which are unheated. The waste, whose thickness should not exceed 5 to 6 millimetres, is easily crushed, especially if not too hard. When the thickness of the waste is greater, and especially when hard, it is passed before grinding into warm water, which by softening facilitates the operation.

A water-supply should always be present at the side of the rolling mill in which the waste is crushed, because it is not uncommon to see the materials ignite through the heat caused by the grinding.

The rolling of the celluloid employed for the manufacture of tubes. The material employed in tube manufacture should be rolled to obtain a very durable substance, and so facilitate the work of the stuffing.

Fig. 49 represents a Decauville Rolling Machine.

The Rolling Mill Installation,

In the example shown for the installation of a celluloid works manufacturing about 725 kilogrammes of nitrocellulose per day, and producing in 10 hours from 1200 to 1400 kilogrammes of unpressed celluloid, 5 rolling mills are necessary, allowing that 35 to 38 kilogrammes of celluloid may be rolled per hour.

This number of machines is not exaggerated, because the grinding of the waste must also be taken into account. The most practical driving system is that by an underground shaft. A table is attached to each rolling mill where the sheets to be placed in the press are cut. This table should have the exact dimensions of the box in which the block is placed, and which measures ordinarily 1374 millimetres long by 663 millimetres wide. In the workshop containing the rolling mills are also found the kneader and a cutting machine by which the new material is cut into cubes or fragments necessary for the manufacture of certain varieties. By this apparatus the waste is also cut up for steeping.

The space occupied by a rolling mill is 3 square metres, that of the kneader with its thermo-siphon 4 square metres. Finally, an ordinary cutting machine takes up 3 square metres.

The steam and water pipes of the rolling mills are fixed in the air and should not be placed above the machines.

COMPRESSION.

The object of compression is to give the rolled sheets a complete cohesion and to obtain an absolutely compact mass. This result is arrived at by compressing the rolled sheets with hydraulic pressure, at the same time heating them. Under the influence of this combined compression and heating, the celluloid is softened and forms a block which is left to cool.

Block Presses.

There are two kinds of block presses in existence which we shall proceed to examine.

The ordinary block press. This press, which is mostly employed, consists essentially of an iron frame in which are fitted steel pillars and a hydraulic cylinder. The pillars, four in number, also support an iron frame which is fastened to them. In the cylinder, which is attached to the lower frame, is a plunger supporting a plate. Upon this plate is a box, hollow in the interior and serving for heating the block which is placed upon a floor situated above the box.

The block is surrounded by a box formed of four sides independent of

each other, and maintained against the walls of the block by binding screws. Above the box is a steel piece which exactly fits the inner surface and presses the enclosed block when the latter is raised up.

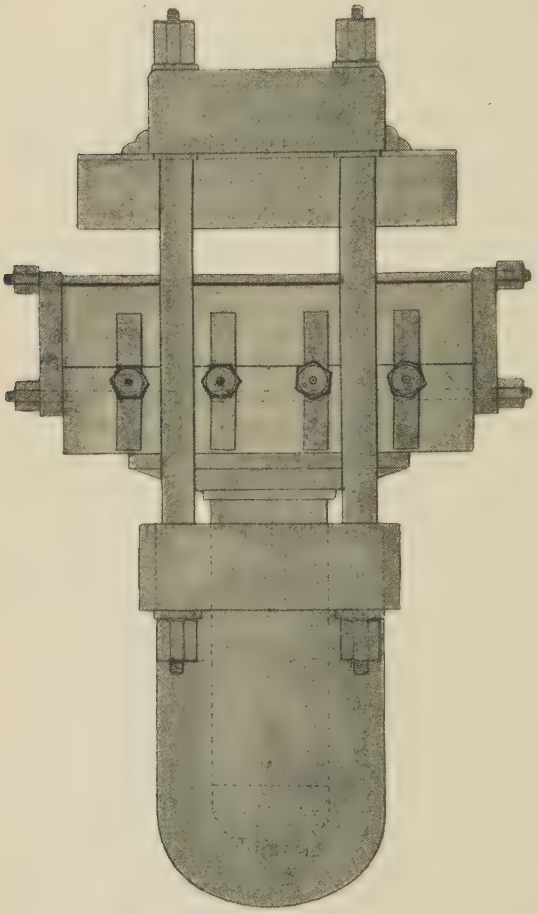


Fig. 50. Block Press (side view).

Two distributors admit the hydraulic pressure (low and high pressure).

The cylinder of the press is placed downwards in the ground.

The heating is brought about by two tubes, which convey steam into the cylinder of the lower box as well as into the part functioning as plunger. These two latter contain water which is heated by the steam tubes. The surplus hot water escapes by one or two pipes. Cold water may also be introduced by the same pipes.

The heating of the press may be performed by a steam pipe 27 millimetres in diameter, from which are branch pipes of 15 millimetres diameter. The tubes penetrating into the interior of the plunger and cylinder are 12 millimetres. The same pipe system may be adopted as in a press to be examined later.

The steam feeding the presses should be under 3·5 to 4 kilogrammes pressure.

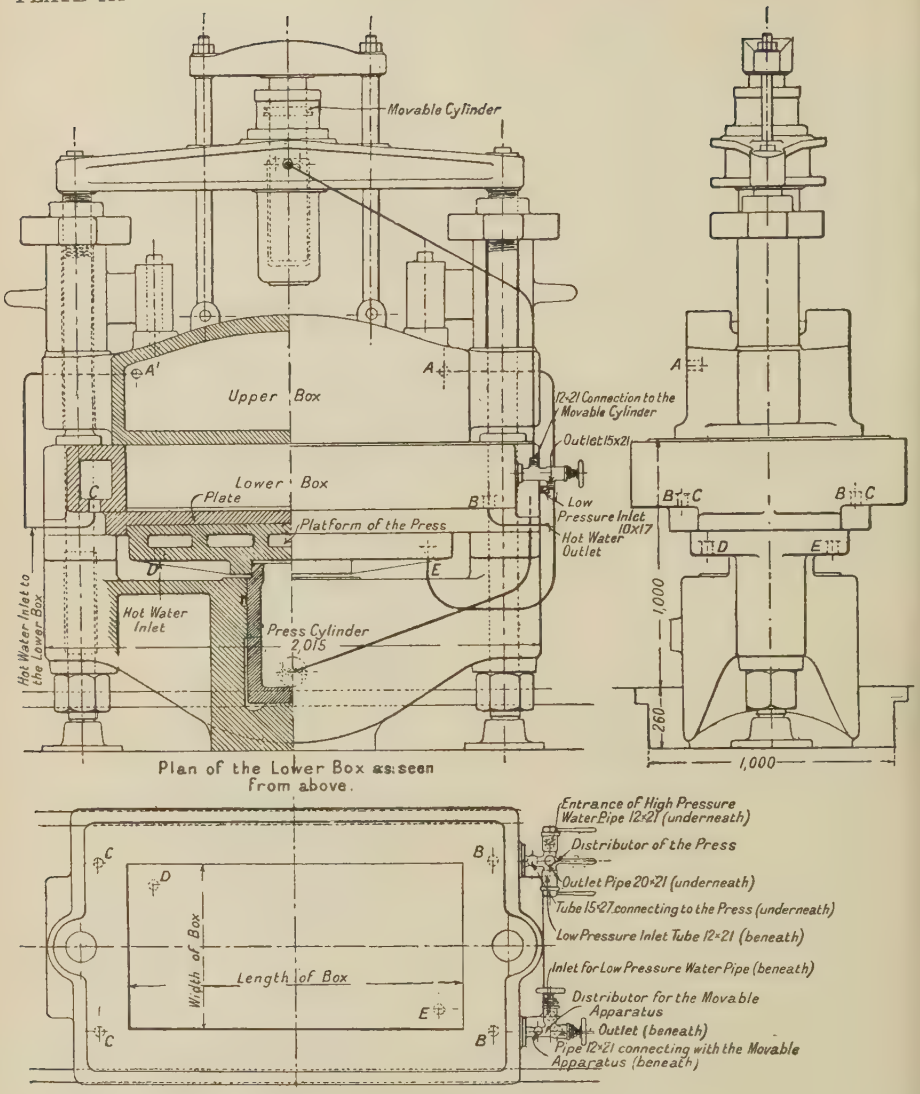
The pipes for cooling the press are usually:

Inlet pipe	23	mm. diameter.
Feeding pipe	15	,, ,,
Pressure distributing pipe	12	,, ,,

The block presses may be heated by hot water.

In an important works, the heating is made by means of large sheet-iron tanks, in which water is warmed by bubbling steam through and thus

PLATE III



Key.

A. Hot Water Inlet to the Upper Box.	C. Hot Water Inlet to the Lower Box.
A' „ „ Outlet from the Upper Box.	D. „ „ „ „ „ Platform.
B „ „ „ „ „ lower „	E. „ „ Outlet from the Platform.

CHAMPIGNEUL'S BLOCK PRESS

To face page 111

raising its temperature to about 90° C. These hot water tanks overhang the presses, and, on account of their elevation, supply the water to the presses direct. From the latter, the water is taken to a collector by a centrifugal pump and returned to the tanks. The hot water thus makes a continuous circle and so promotes very uniform heating.

The working of the press. The material having been rolled and worked into sheets is taken to the press room where the press to be charged is furnished with a fluted plate, the anterior side of the box being removed. Care must be taken to turn on the steam which heats the water contained in the cylinder and plunger. This being done, four workmen place the box, containing the sheets for pressing, upon the frame, the bottom of the box being on the upper surface of the plate. The fore part of the box, which is adjusted for this purpose, is withdrawn, and the material pressed upon the plate. The two sides of the box are made to approach by tightening the binding screws, then the anterior side of the box is placed in position and fitted to the box by the screws provided.

The low pressure is turned on and the press mounted, having previously placed upon the material to be pressed a sheet of zinc, which has the dimensions of the box and whose four sides are bent at right angles so as to surround entirely the upper part of the block and prevent loss of material during heating. When the press has mounted, the high pressure is turned on. (150 kilogrammes per square centimetre.)

The block, having been pressed, is released by unscrewing the binding screws and disengaging the sides of the box which adhere to the material. It only remains to place the block upon a special truck which may be raised or lowered at convenience. (Fig. 51.)

New types of press. For some years, presses have been constructed with the object of diminishing the manual labour necessitated when pressing with the older types.

The newer press consists of a lower plunger of short stroke supporting a platform upon which a fluted iron plate is directly placed, the object of whose striations is to cause the celluloid placed on this plate to adhere. Surrounding this platform is a hollow iron piece of rectangular section, which plays the part of the box in the preceding press system.

We may heat this piece which is fixed and traversed by two pillars; by the latter slides an iron block, which just rests upon the fixed block and plays the part of plunger, the whole of it not penetrating into the box. In a cylinder situated at the upper part of the press, and secured to the iron block by two arms, works a piston of small diameter. By turning hydraulic pressure upon this piston, the iron block forming the top of the press may be moved and so play the part of plunger.

Two lips placed on the periphery of the pillars prevent the aforementioned piece from being raised when the platform just presses the block against it.

Plate III. shows the details of a press by the firm of Champigneul.

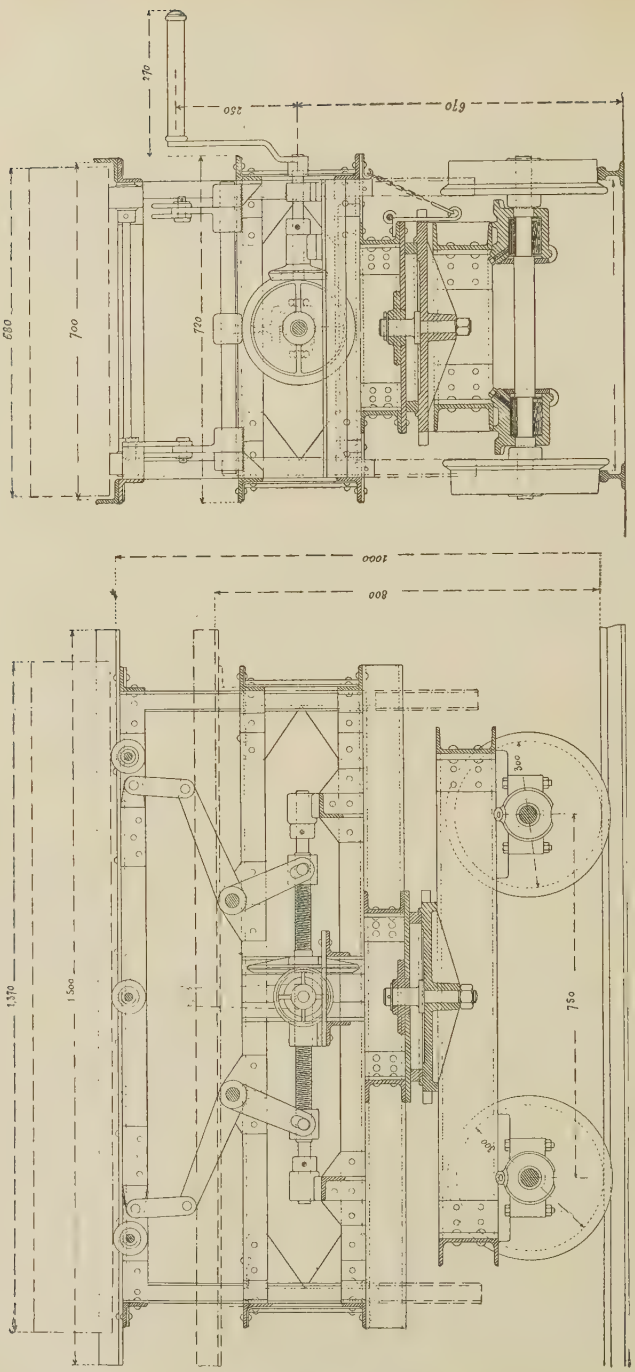
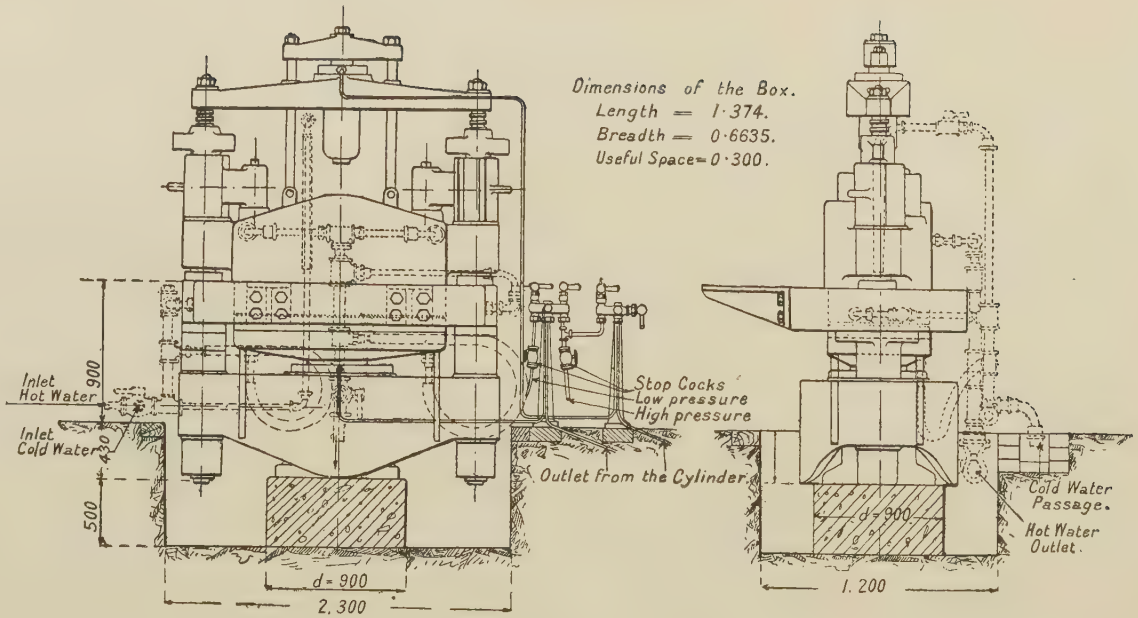


FIG. 51. Truck with Adjustable Platform.



DECAUVILLE'S BLOCK PRESS: POWER 200 TONS

To face page 113

Plate IV. represents the installation of a Decauville block press.

The working of this press. The top of the press forming the plunger being raised, the platform, which should support the plate as far as the upper level of the box, is mounted by means of pressure.

The block to be pressed is placed with its plate upon the truck already noticed, which is raised to the height of the box. The block is caused to slide upon the press platform, which is then lowered by emptying the lower hydraulic cylinder. The upper cylinder is also emptied, causing the part of the press playing the rôle of plunger to descend. The two lips are adjusted round the pillars, thus preventing the piston from remounting, and the block is raised so as to press against the piston.

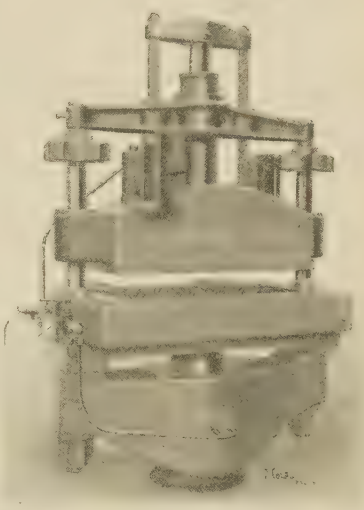


Fig. 52. A Recent Type of Block Press.

As may be judged, the work necessary for loading the block is much reduced in this system.

For releasing from the press, pressure is turned on in the upper hydraulic cylinder, the lips being previously removed from the pillars. The piston forming part is elevated, and it only remains to raise the block to the upper level of the box.

This press system presents over the older type the advantage of diminishing much of the manual labour necessitated during compression. Moreover, the older presses do not admit of lateral heating, from which it follows that the edges of the blocks are not always welded.

Heating the press. The block should be heated at a temperature necessary for completely softening the material; it is when in this semi-fluid condition that the hydraulic pressure exerts its entire effect.

It is, nevertheless, necessary not to overheat, since at a certain temperature the material decomposes and may produce, besides loss, very serious accidents. It is unnecessary in any case to exceed 100° C. Certain firms only heat their presses to 70° C.; others as far as 85° and 90° C. The temperature is recorded by two thermometers placed in tubes situated in the walls of the piston section and in the cylinder portion. These tubes are in direct contact with the water contained in the space of these two pieces. The temperature thus indicated is not the actual one, because it only informs us as to the possible temperature of the block sides. According to our experiments it was necessary to heat the block from about 85° to 90° C. for 6 to 7 hours.

We shall examine two examples of heating, one at 75° and the other at 90° C. In these trials two tubes were placed traversing the block throughout its

length. The tubes were placed in the interior of the block and in contact with the material. Each of these tubes contained a thermometer immersed in an oil environment. The observations were taken every 15 minutes. As one may see, great differences exist in the two curves. (Figs. 53 and 54.)

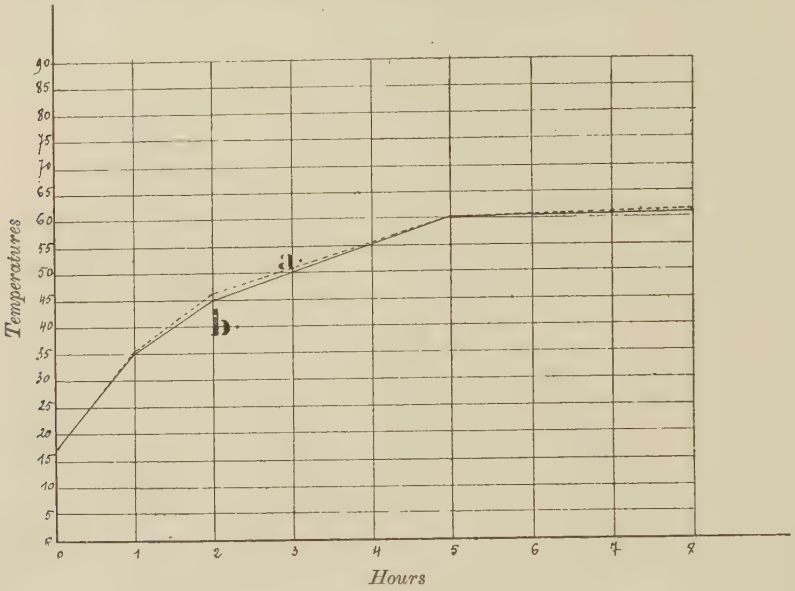


Diagram I. Fig. 53.
Steam pressure, 3·200 kil. Exterior heating, 75°. Duration of heating, 8 hours.

In curve No. 1, Figure 53, the block was internally heated to 50° C. after 3 hours' heating. At the end of 5 hours' heating the temperature was 60° C., and did not increase in spite of a further 3 hours' heating.

In curve No. 2, Fig. 54, after 3 hours' heating 60° C. were attained, and 80° were reached after 5 hours. This limiting temperature only increases a few degrees during the 3 last hours of heating.

Of necessity, in this last trial, the material is better welded than in the first case, and that because the material is better softened.

In conclusion, we believe it advantageous to heat at the temperature we have indicated and for a period of 8 hours.

Cooling the press. The material being fluid and also well consolidated, the steam inlets are closed and the water ones opened so that the block may solidify by cooling while preserving its homogeneity.

How long should the cooling process occupy? This period depends mainly:

(1) On the temperature to which the press has been heated.

(2) On the temperature of the cooling water employed.

The colder the water, the shorter the cooling period. In summer a longer time should be allowed. With water possessing an average temperature of 9

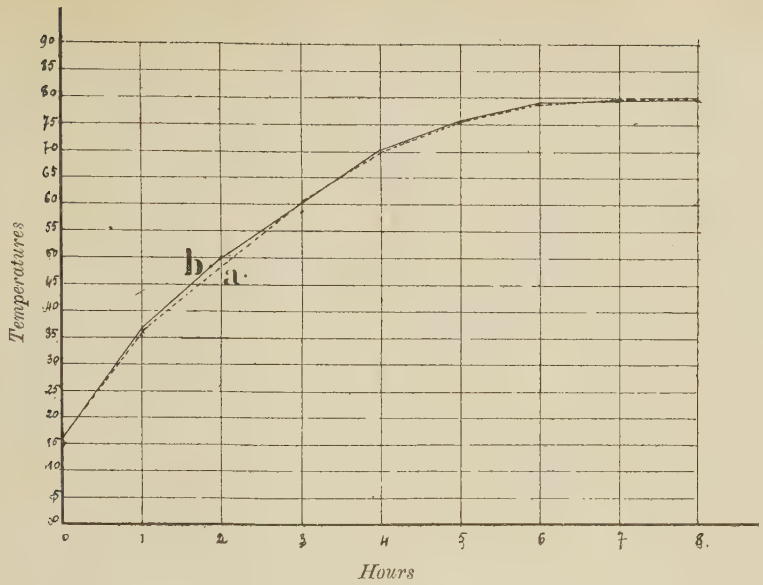


Diagram II. Fig. 54.
Steam pressure, 4·500 kil. External heating to 90° C. Duration of heating, 8 hours.

to 10 degrees in winter and 13 to 14 degrees in summer, 8 hours should be allowed for winter cooling and 10 hours for summer.

Moreover, according to the two following diagrams it will be of advantage

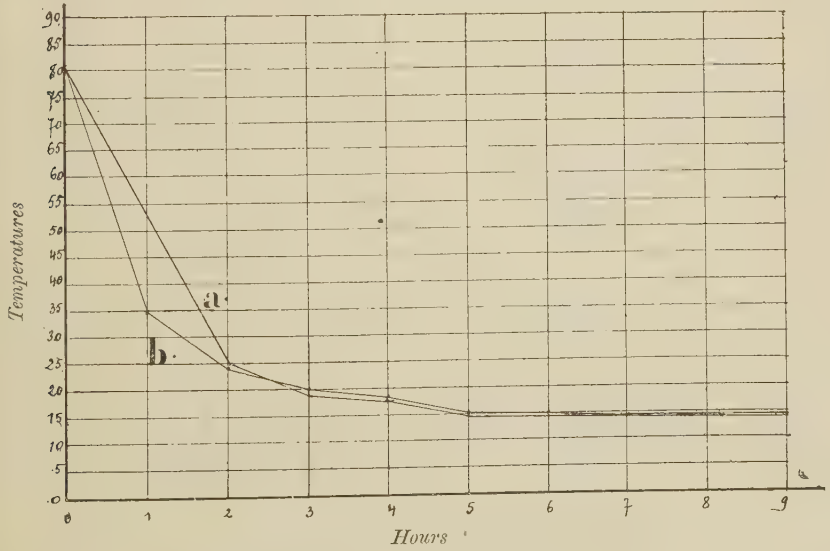


Diagram III. Fig. 55.
Water temperature, 9·7°. Duration of cooling, 9 hours.

to consider the cooling process. These two cooling experiments were commenced from two final heating temperatures.

In Diagram III., Figure 55, note that the temperature falls abruptly from 80° to 26° in 2 hours; afterwards 6 hours are necessary to reach 13° and 15° C. The top of the block is seen to cool more rapidly than the lower portion.

In Diagram IV., Figure 56, there is a fall from 60° to 21° in 2 hours, then it terminates at 14° C.

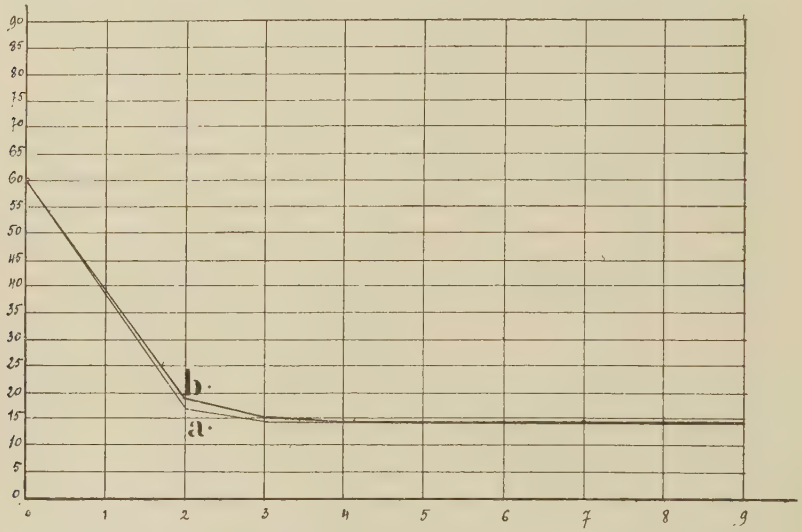


Diagram IV. Fig. 56.
Water temperature, 9·9°. Duration of cooling, 9 hours.

If the cooling be continued, the temperature would only be lowered to 11 or 12 degrees after 3 hours of supplementary cooling.

Therefore as a summary we have:

Heating	8 hours.
Cooling	7 to 8 hours.

INSTALLATION OF THE PRESS HOUSE.

According to the above, a block occupies the press for a maximum of 16 hours.

When heating the presses day and night, 5 presses are necessary for compressing the product obtained by steeping 725 kilogrammes of pulp, *i.e.* 8 blocks. It will be preferable to install 6, because this would permit the utilisation of a portion of the waste produced daily during manufacture.

These presses occupy a space of:

Length	2·500 metres
Breadth	1·500 „

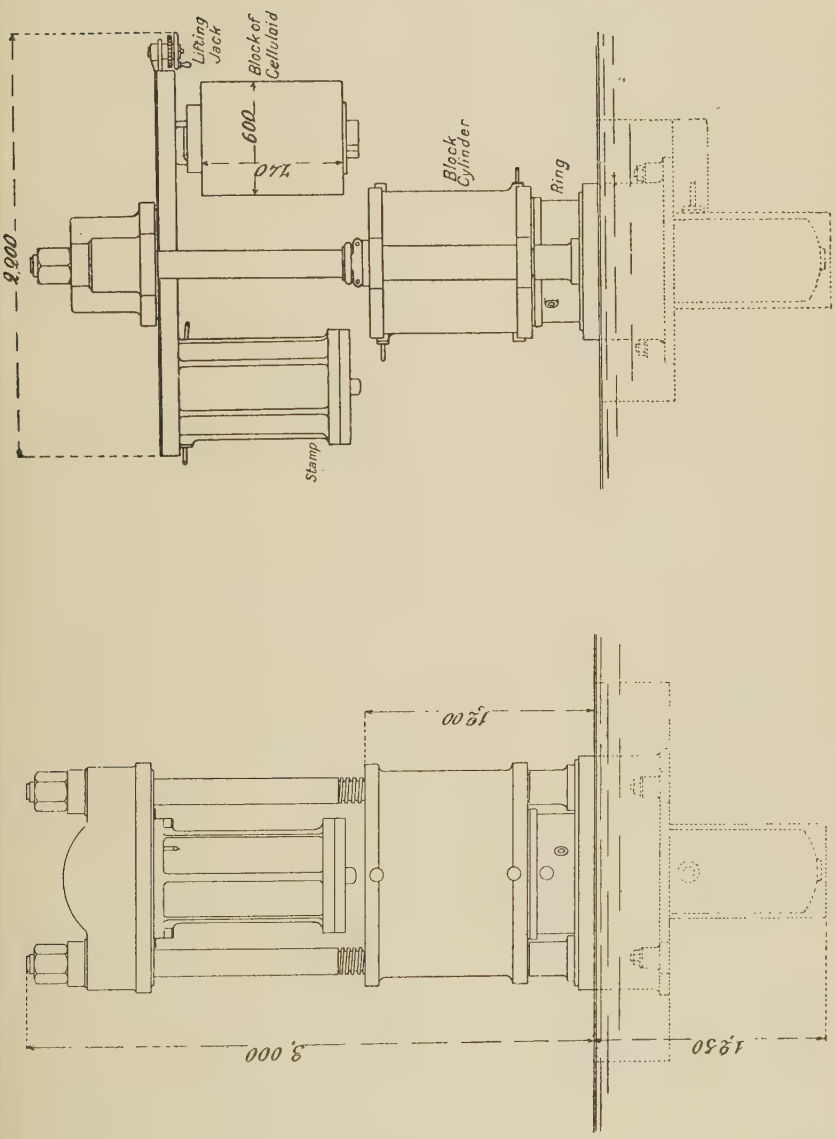


Fig. 57. Vertical Press for Cylindrical Blocks.

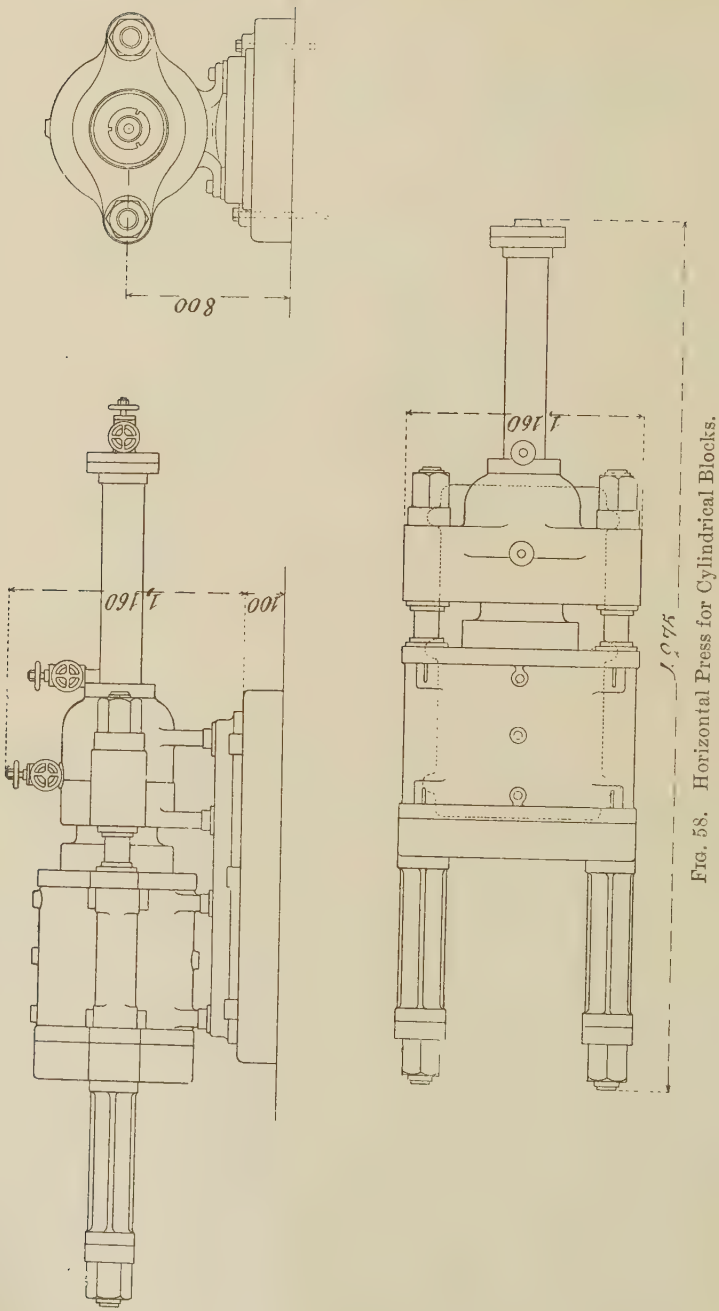


Fig. 58. Horizontal Press for Cylindrical Blocks.

With a Decauville truck the blocks may be transported.

The complete cooling of the block may be made by withdrawing it from the press and placing in a masonry vat in which water constantly circulates.

The block is taken from the press and placed on a truck, from which it is taken by 4 clutches which just lodge in the hollows provided in the plate. These clutches are secured by strong chains to a sliding platform which carries the block to the cooling vat.

At the present time presses for cylindrical blocks are also made. Fig. 57 represents a press constructed by the firm Grether, of Fribourg, having a total output of 170,000 kilogrammes. This same firm also construct cylindrical block presses composed of a frame, and a cylinder for containing the celluloid which a plunger may displace vertically; a stamp penetrates into this cylinder and compresses the block, which is removed by a lifting jack (Fig. 58). These cylindrical blocks may afterwards be cut into sheets of great length.

Re-pressing the material. All the materials used for the manufacture of agates, ivories, veined articles, &c., are compressed anew in order to consolidate the designs executed. In addition, materials having defects, principally wrinkles, are also re-pressed. The block is cut into small thicknesses and subjected to a second compression or re-pressing. After several compressions the material finally loses its colours.

Compression accidents. When the material is overheated, and especially when irregularly heated, there may be produced violent temperature elevations which burn the material. The latter then presents discoloured patches giving a very bad effect.

The material may also be badly welded, a defect attributed to deficient heating.

Complementary cooling. Certain firms follow press cooling by a complementary cooling. The blocks are either laid on tables over which water flows or entirely immersed in vats constructed of masonry. In a good press cooling, this practice is useless and the block may be cut without the material being wrinkled.

Very often the material laid on the tables is pierced by small holes, due to the surrounding temperature causing the expansion of the alcohol which is disseminated throughout the block mass.

CHAPTER X

CUTTING AND DRESSING

Cutting.

Cutting the material. When the block has been sufficiently pressed and cooled, it is submitted to the cutting process. For this purpose a cutting machine is used known under the names of planing machine or cutting machine.

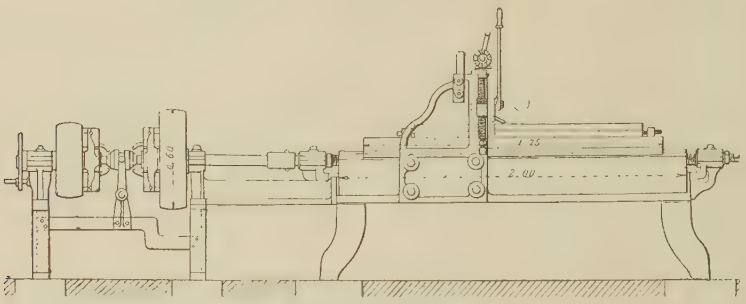


FIG. 59. The Planing Machine.

The planing machine consists of a rectangular cast-iron frame upon which are two horizontal and parallel sliding faces. Upon these sliding faces just lodges a

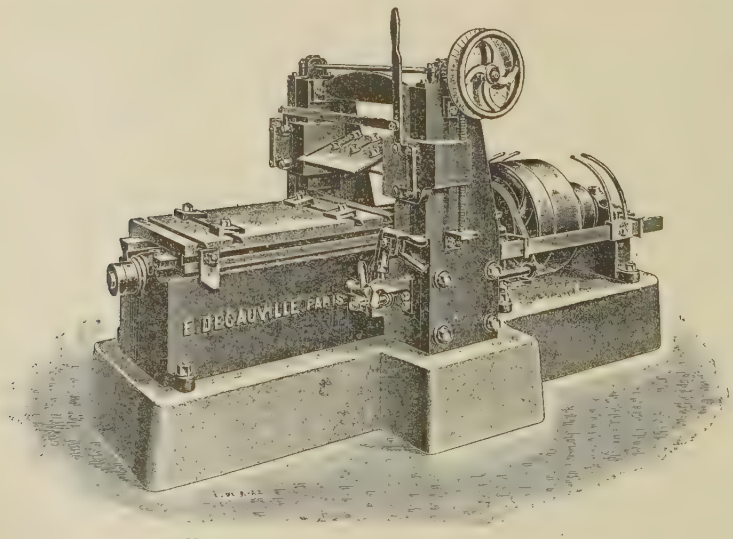


FIG. 60. Decauville Cutting Machine.

plate provided with an endless screw placed underneath. This endless screw carries at its extremity two pulleys of different diameters rotating in opposite directions, and each capable of being thrown into gear by means of a driving lever placed at the head of the apparatus. The larger pulley when started serves to advance the plate carrying the block, and brings it into contact with the knife. When the sheet has been cut, the smaller pulley is thrown into gear, and brings the platform back to its former position.

The cutting of the sheets is made by a large knife with a steel blade, placed obliquely upon the knife carrier. The latter consists of a piece of cast iron of rectangular form. This cutter carrier is secured by two cross-bars, and is connected by a system of two endless screws to a shaft worked by a crank. Upon this shaft is a dial indicating by what amount the knife has descended.

The block is secured upon the platform of the planing machine by two pieces fixed on this platform, between which the plate lodges. Binding screws traverse these pieces, and firmly secure the block by tightly pressing the plate.

An arrangement also exists by which cramp irons fit into channels prepared in the plate.

Fig. 60 shows a type of cutting machine constructed by the firm of Decauville, and Figure 61 represents a cutting machine, with automatic descent of the cutter-head, made by the firm of Morane Jeune.

The mode of working the planing machine. The block having been firmly fixed upon the platform is then cut. For that purpose the knife is lowered

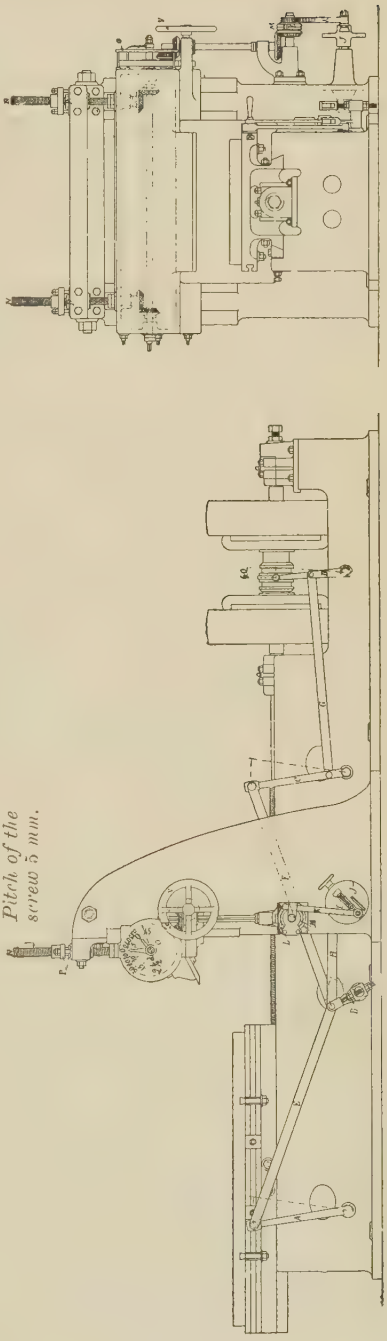


FIG. 61. Cutting Machine with Automatic Descent of the Cutter-head.

by turning the crank on the right of the machine, so as to place the knife in contact with some millimetres of the material (1 or 2). The planing machine is then thrown into gear, and the knife penetrates into the top of the block. An irregular sheet is thus obtained, and the operation is repeated until the surface of the block is perfectly horizontal.

It is then that the cutting proper commences. The division corresponding to the thickness of the sheet desired to be cut is first chosen. The dial provided on the planing machine is graduated into 36 divisions, each of which is 10. Between each of the large divisions are 10 sub-divisions, these corresponding to $\frac{2}{100}$ in consequence of the tens carried on the dial corresponding to $\frac{2}{10}$. Let us consider, for example, the cutting of a block into $\frac{14}{100}$; we take 7 small divisions on the dial. If the sheet is to be to $\frac{28}{100}$, we take one large and four small divisions. A difficulty experienced in cutting is to give such a thickness to the sheet cut that the latter, after drying, shall have the desired thickness. The shrinking which takes place during drying is unequal; the less the thickness, the more uniform the shrinkage.

In order to cut sheets from $\frac{10}{100}$ to $\frac{28}{100}$, the thickness is increased by $\frac{2}{100}$. From $\frac{3}{10}$ to $\frac{5}{10}$, the increase is $\frac{5}{100}$. From $\frac{5}{10}$ to $\frac{7}{10}$, the increase is $\frac{7}{100}$. Finally, from $\frac{7}{10}$ to $\frac{10}{10}$ and over, $\frac{1}{10}$ is added. Note however that these figures are liable to variation according to the mode of working.

The work performed by a planing machine is very irregular, and depends on the thickness to which the cutting is made. The less thick the sheets, and the more limited the work. Generally it is calculated that a machine with one operator and assistant may cut in 10 hours:

100 kilogrammes of sheets		$\frac{3}{10}$ thick.
25	,,	,, from $\frac{35}{10}$ to $\frac{45}{10}$,,
350	,,	,, ,, $\frac{45}{10}$ to $\frac{100}{10}$,,
650	,,	,, ,, 10 mm. to 20 mm. thick.

Each cutting operation gives some waste, the amount of which varies according to the skill of the operator and the tenacity of the material. Moreover, during the cutting operation, a fairly considerable evaporation of alcohol is produced. In the Table on page 123 we give some data concerning this matter.

It will be seen that the thickness causes the weight of the waste to vary; also the evaporation of alcohol during the cutting process is irregular. For 100 kilogrammes of material cut, the average waste may be reckoned at 90 to 12 per cent. As for the evaporation it is from 5 to 8 per cent.

THE CUTTING OF RODS.

Originally, rods were made by the stuffing, a process to be dealt with later. Afterwards a method was devised for cutting rods from blocks by means of a kind of punch. The blocks are cylindrical and mounted in a species of lathe. In front of the block is a tool maintained in a movable carriage. By the rotation of the block and the penetration of the tool into it, a rod of very great length is obtained; it only remains to divide up the latter. This

system of cutting would necessitate in the first place the use of cylindrical presses, and would possess the inconvenience of giving a small output, while demanding great skill on the part of the operator. Lastly, the amount of

Thicknesses cut	Weight of the block	Weight of the sheets cut	Weight of the waste	Loss by evaporation
	k.	k.	k.	k.
$\frac{10}{10}$	108	81	15	12
$\frac{15}{10}$	144	121	14	9
$\frac{18}{10}$	145	117	18	10
$\frac{20}{10}$	136	120	11	5
$\frac{22}{10}$	153	123	21	12
$\frac{25}{10}$	158	140	10	8
$\frac{30}{10}$	150	123	17	10
$\frac{35}{10}$	151	120	18	13
$\frac{40}{10}$	146	125	12	9
$\frac{45}{10}$	145	130	9	6
$\frac{50}{10}$	139	116	12	11
$\frac{55}{10}$	142	120	14	8
$\frac{60}{10}$	145	121	13	11
$\frac{65}{10}$	134	113	12	9
$\frac{70}{10}$	143	118	17	8
$\frac{75}{10}$	154	118	23	13
$\frac{80}{10}$	170	150	12	8
$\frac{85}{10}$	147	113	20	14
10 mm.	172	141	21	10

waste is large. This system has therefore been superseded by one actually employed in every works.

The same planing machine is used as for sheet cutting, the knife being replaced by a piece carrying special tools. These tools consist of a steel piece whose centre is pierced by a circular orifice. These types of centre punches are provided with a square rod. The tools, to the number of 5 or 6, are fixed into an iron bar of square section which is joined to a perpendicular part lodged in a mortise and firmly secured by two bolts.

The piece, into which is fitted the tool carrier, is worked by an endless screw which causes it to move in a horizontal direction. Finally, by means of a crank, the tool carrier may be moved in a vertical direction. Each tool is accompanied by a small blade mounted on a bar which is fixed to the tool carrier.

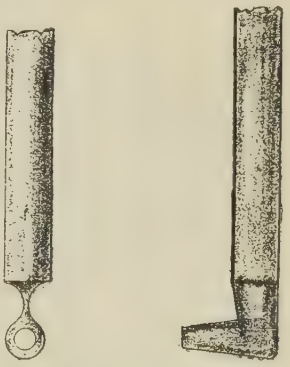


FIG. 62. A Rod Tool.

The regulation of tools. Let us suppose a set of 6 tools. As shown in the scheme below, there is a knife between each tool; tools and knives are

placed in such a way that they work conjointly. An oblique direction is adopted. The first knife removes a regular band of material; the first tool just cuts the rod at the part scooped out by the knife. The second blade hollows a new furrow where the second tool just cuts, and so onwards. The knife therefore serves to remove the part remaining round the space which was occupied by the rod.

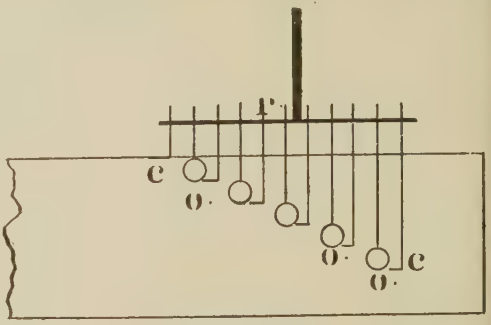


Fig. 63. Scheme for Rod Cutting.
c. Knife. o. Rod Tool.
r. Tool Carrier.

Mode of cutting. The tool carrier being in position, the tools and knives are fixed on it in an oblique line. Let us suppose that the first blade is placed 27 millimetres from the base of the tool carrier. The first tool is placed at a height permitting a rod to be cut regularly. Let us suppose that rods of $\frac{30}{10}$ diameter have to be cut; the first knife being placed at 27 millimetres, the upper part of the tool will be at 27 millimetres plus some tenths, and the base of the tool will be at 30 millimetres plus some tenths. The same applies to every other tool. This being done, the tool carrier is placed at the right of the block so that the first knife may just cut a strip of 1 millimetre all along the block. The thickness to be cut is regulated by a crank, which allows the tool carrier to rise or fall. The tool carrier is displaced a sufficient amount horizontally so that the knife cuts a second strip similar to the first. For this operation the dial, which denotes 12 divisions as well as some half divisions, serves as guide.[1]

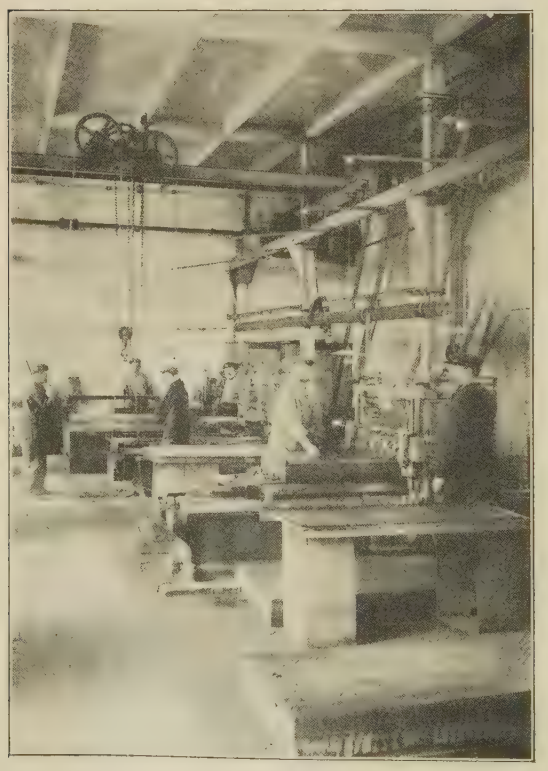


Fig. 64. The Cutting Room.

[1] Upon the given scheme of cutting, we have intentionally increased the depth to which tools and knives work.

By thus continuing to advance, the tool penetrates into the block and cuts a rod from it. The essential point is, that the tool and knife should be so regulated that the rods have a circular section and the waste reduced to a minimum amount.

When the tool carrier has arrived at the edge of the block, it is returned to the starting-point and the work recommenced by lowering the same.

The rules for setting the tools and knives cannot be given, but it may be admitted that 5 millimetres of depth per tool are necessary. Moreover, the upper part of the rod should be just flush with the surface of the block.

As in the case of sheets, it is always necessary to cut rods of diameter a little greater than that possessed after drying. For rods up to 10 millimetres in diameter, $2\frac{1}{2}$ to $\frac{3}{10}$ excess is usually allowed; above 5 to $\frac{6}{10}$ or more may be taken.

The tools bear numbers corresponding to the diameter. They should be frequently ground, and in the best way, since tools indifferently sharpened give rods of varying diameters.

It is necessary to state that for 100 kilogrammes of undried rods, 70 to 90 kilogrammes of waste are made according to the thickness of the rods cut and also according to the skill of the operator.

The following Table is a summary of information concerning rod-cutting:

The Cutting of Rods.

Weight of the block	Diameter of the rods	Weight of the newly cut rods	Weight of the waste	Loss by evaporation	Tool	Division
k.		k.	k.	k.		
130	$\frac{30}{10}$	66	54	10	$3\frac{1}{2}$	$6\frac{1}{2}$
131	$\frac{30}{10}$	64	58	9	$3\frac{1}{2}$	$6\frac{1}{2}$
126	$\frac{33}{10}$	63	53	10	4	7
148	$\frac{40}{10}$	78	58	12	$4\frac{3}{4}$	$8\frac{1}{2}$
130	$\frac{40}{10}$	73	48	9	$4\frac{3}{4}$	$8\frac{1}{2}$
140	$\frac{45}{10}$	76	54	10	$5\frac{1}{4}$	$9\frac{1}{2}$
127	$\frac{45}{10}$	60	56	11	$5\frac{1}{4}$	$9\frac{1}{2}$
139	$\frac{50}{10}$	75	54	10	$5\frac{3}{4}$	$10\frac{1}{2}$
130	$\frac{58}{10}$	70	51	9	$6\frac{1}{2}$	12

After the cutting process the waste is clipped either by hand shears or by mechanical cutters.

A planing machine in 10 hours can cut:

40 kil. of rods of $\frac{18}{10}$ to $\frac{22}{10}$ in diameter.
100 „ $\frac{25}{10}$ to $\frac{30}{10}$ „
200 „ $\frac{32}{10}$ to $\frac{45}{10}$ „
275 „ $\frac{45}{10}$ to 10 mm. „

INSTALLATION OF THE CUTTING PLANT.

In the example of the production from nitration of 725 kil. of nitrocellulose, 8 blocks were made in 10 hours, destined to yield 800 kilogrammes of dry celluloid. In the limit a single planing-machine may therefore be employed, especially if rods are not manufactured. When rods have also to be cut, two machines are necessary.

The latter occupy a space of 6 square metres.

THE DRYING OF CELLULOID.

After cutting the material it is dried, the object being to evaporate the retained alcohol and other solvents, as also to impart rigidity to it.

Before placing the material in the drying chambers, it is expedient to let it dry in the open air. For this purpose the sheets are laid one by one upon

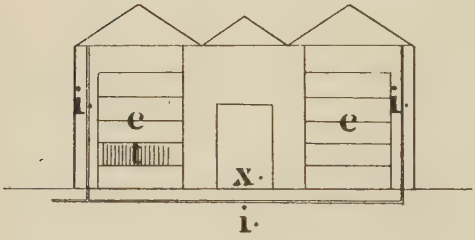


Fig. 65. A Drying Chamber for Celluloid (section).

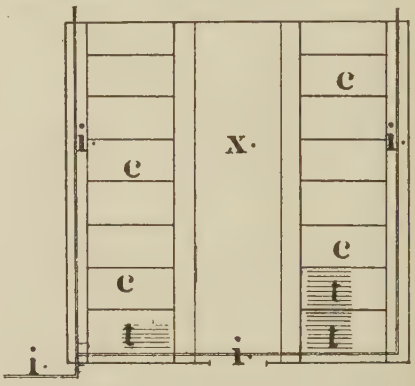


Fig. 66. A Drying Chamber for Celluloid (plan).

x. A service passage.
t. Sheets which are drying.
c. Cases for storing the celluloid to be dried.
i. Steam pipes heating the drying chamber.

wicker-work of soft wood, and allowed to remain for 3 to 8 days according to the thickness of the material. The thicker the sheets, and the longer the period before placing them in the dryer. If they are placed immediately in the drying chamber, an evaporation of the alcohol is brought about by the heat thus producing small internal holes which give a very bad effect.

The drying chambers. These drying chambers are built of masonry. Inside are iron cases in which the sheets of celluloid for drying are stored. Each sheet is placed edgeway along its length, and is separated from its neighbour by wicker-work. The heating is performed by steam conveyed by a system of steam pipes or by carriers. The steam pipes may be arranged upon the walls or at the basement. (See both systems of drying chambers.)

To what temperature should the drying chambers be heated? The quicker the celluloid is dried, the more time gained and the greater the profit.

There is, however, a limiting temperature which should never be exceeded. For thickness not greater than 1 centimetre, the drying chambers may be heated to 50° C. For large thicknesses exceeding 10 millimetres, the drying chamber should not be heated to more than 30° C. for reasons already pointed out.

Duration of drying. The drying varies with the thickness of the material. We indicate below the time required for drying different thicknesses.

Temperature of the Drying Chamber, 50° *C.*

Thicknesses of	$\frac{10}{100}$ to $\frac{23}{100}$	1 day.
,,	$\frac{24}{100}$,, $\frac{55}{100}$	2 days.
,,	$\frac{56}{100}$,, $\frac{10}{10}$	5 ,,
,,	$\frac{11}{10}$,, $\frac{25}{10}$	11 ,,
,,	$\frac{26}{10}$,, $\frac{32}{10}$	13 ,,
,,	$\frac{33}{10}$,, $\frac{40}{10}$	17 ,,
,,	$\frac{41}{10}$,, $\frac{50}{10}$	22 ,,
,,	$\frac{51}{10}$,, $\frac{65}{10}$	25 ,,
,,	$\frac{66}{10}$,, $\frac{75}{10}$	28 ,,
,,	$\frac{76}{10}$ and over	32 to 35 ,,
Large thicknesses		50 ,,

Thicknesses of 1 to 2 centimetres in the dryer at 30° C. 50 days.
,, ,, ,, 50° C. 150 ,,

The drying of rods and tubes. In many works rods and tubes are dried in the open air, and require a long drying period.

When the materials are liable to become flattened, we cannot utilise the drying chambers at 30°, and so employ not heat but aeration. Rods and tubes may be dried fairly rapidly by air displacement. We refer the reader to the drying chamber scheme below.

When drying with this system it is necessary to allow for varying drying periods as follows:

Diameters of	$\frac{1}{10}$ to $\frac{20}{10}$	16 days
,,	$\frac{21}{10}$,, $\frac{30}{10}$	19 ,,
,,	$\frac{31}{10}$,, $\frac{40}{10}$	21 ,,
,,	$\frac{41}{10}$,, $\frac{50}{10}$	23 ,,
,,	$\frac{51}{10}$,, $\frac{60}{10}$	25 ,,
,,	$\frac{61}{10}$,, $\frac{70}{10}$	26 ,,
,,	$\frac{71}{10}$,, $\frac{80}{10}$	28 ,,
,,	$\frac{81}{10}$,, $\frac{90}{10}$	29 ,,
,,	$\frac{91}{10}$,, 10 mm.	30 ,,

We have devoted some experiments to rods of different diameters placed in our drying chamber. The next Table contains the summary of the variations undergone during the drying operation.

An Experiment in Drying.

Diameter of the rods	Weight at cutting	Weight found after							Loss per cent.	Drying complete after
		2 days	4 days	9 days	14 days	19 days	21 days	30 days		
	k.	k.	k.	k.	k.	k.	k.	k.		
Rods of $\frac{28}{10}$	104·0	100·0	98·0	96·0	95·5	94·5	92·0	—	11·5	21 days
„ $\frac{28}{10}$	110·4	107·8	105·4	103·4	102·6	101·2	100·8	—	9·42	21 „
„ $\frac{50}{10}$	115·2	113·2	110·6	108·4	107·6	106·2	105·0	—	8·85	21 „
„ $\frac{50}{10}$	115·0	121·3	117·8	115·0	110·4	106·4	105·8	104·9	8·78	30 „

Installation of the drying chambers. These should be installed in the way we have previously indicated.

With the drying period recommended, the number requisite should be:

2 drying chambers heated at 50° C.
and 2 heated at 30° to 35° C.

For rods and tubes, 1 cold chamber will suffice.

The dimensions of the drying chamber should be:

Length	6500 mm.
Width	5500 „
Height	4500 „

DRESSING.

Dressing celluloid sheets. On account of the sojourn of the sheets in the drying chamber, they shrink and warp a little. The sheets must, therefore, be planed again, an operation known as dressing.

At the outset of the celluloid manufacture, the sheets were placed in a zinc box having slightly elevated edges. Water at 95° C. was turned on, and the sheet to be dressed was allowed to remain in contact with the water a short time. The latter was then run off. The sheet was next softened by heat and fitted exactly to the floor of the box. Cold water sufficed for cooling, and sheets were obtained fairly well dressed.

To-day, pressure is used conjointly with heat for dressing celluloid sheets. Special presses, known as "Dressing Presses," are used.

The latter consist of a foundation, sunk in the ground, carrying a cylinder. The cylinder is furnished with a piston bearing steel plates each guided by two or four pillars. These plates are hollow, and may receive steam or water at convenience by means of a pipe. Each plate is separated from the preceding one by a space in which the sheets for dressing are placed. The distance existing between the plates is secured by racks, upon which the press plates rest. The latter, whose number is variable (5, 7, 10, or 12), are surmounted by a cap fixed upon the pillars. This press may work at both low and high pressure.

Upon the figure representing the dressing press, the section into which the steam or cooling water arrives is not shown.

The working and management of the dressing press. The block to be dressed is divided into a certain number of sections (as many sections as plates), whose sheets are placed between two brass plates. The sheets are then placed between the press plates. The press is next heated to a temperature varying from 65 degrees to 70 degrees, but not exceeding the latter. The heating is largely a question of custom.

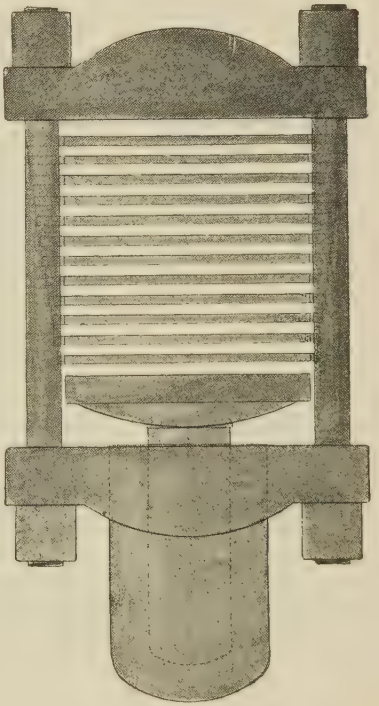


FIG. 67. Dressing Press.

When the press is hot the plates are raised by the low pressure, and then the high pressure is turned on. By heat and pressure combined, the sheets soften and assume the surface of the plates. When the softening is judged sufficient the steam is shut off and a current of cold water substituted, whereby rigidity is imparted to the sheets. After the cooling process is completed, the hydraulic cylinder is emptied and the pressure released.

The sheets are fit to be delivered to the store after being submitted to a toilette consisting in properly trimming the edges. In many works, softening is commenced before dressing, especially for fairly thick sheets. This softening is brought about by steeping the sheets in boiling water. The surface of the sheets should be dried before pressing.

A block of 100 kilogrammes of sheets may be pressed in 35 to 40 minutes with a press carrying 8 plates. The duration of heating is from 20 to 25 minutes, that of cooling, 15 to 20 minutes. The complete operation lasts an hour.

Installation of the dressing press. This press occupies but a small space, viz. 4 square metres.

The above is often installed in the block press chamber.

The usual dimensions of the press plates are:

Length	1370 to 1400 mm.
Width	650 to 700 ,,
Height	58 ,,

with a working space of 50 to 55 millimetres.

With dressing presses having two pistons, the latter, after a little usage do not always work simultaneously, thereby straining the press. This remark

also applies to double piston block presses. A table, sufficiently large and placed near the press, serves for charging and discharging the plates.

The dressing of rods. Rods are usually dressed by steeping them in baths containing boiling water, followed by hand-rolling on a cast-iron table. Owing to the rotation, the heated rods assume a rectilinear posture which is preserved on cooling. In certain works rollers are used, which execute the dressing in a more perfect manner.

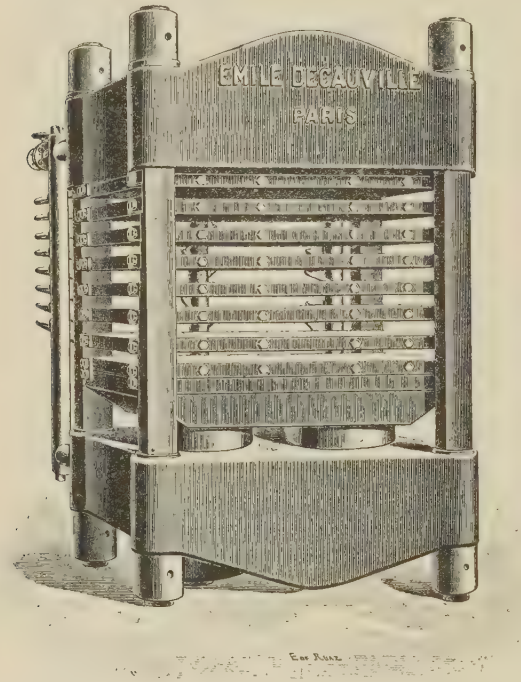


FIG. 68. Dressing Press with Two Pistons.

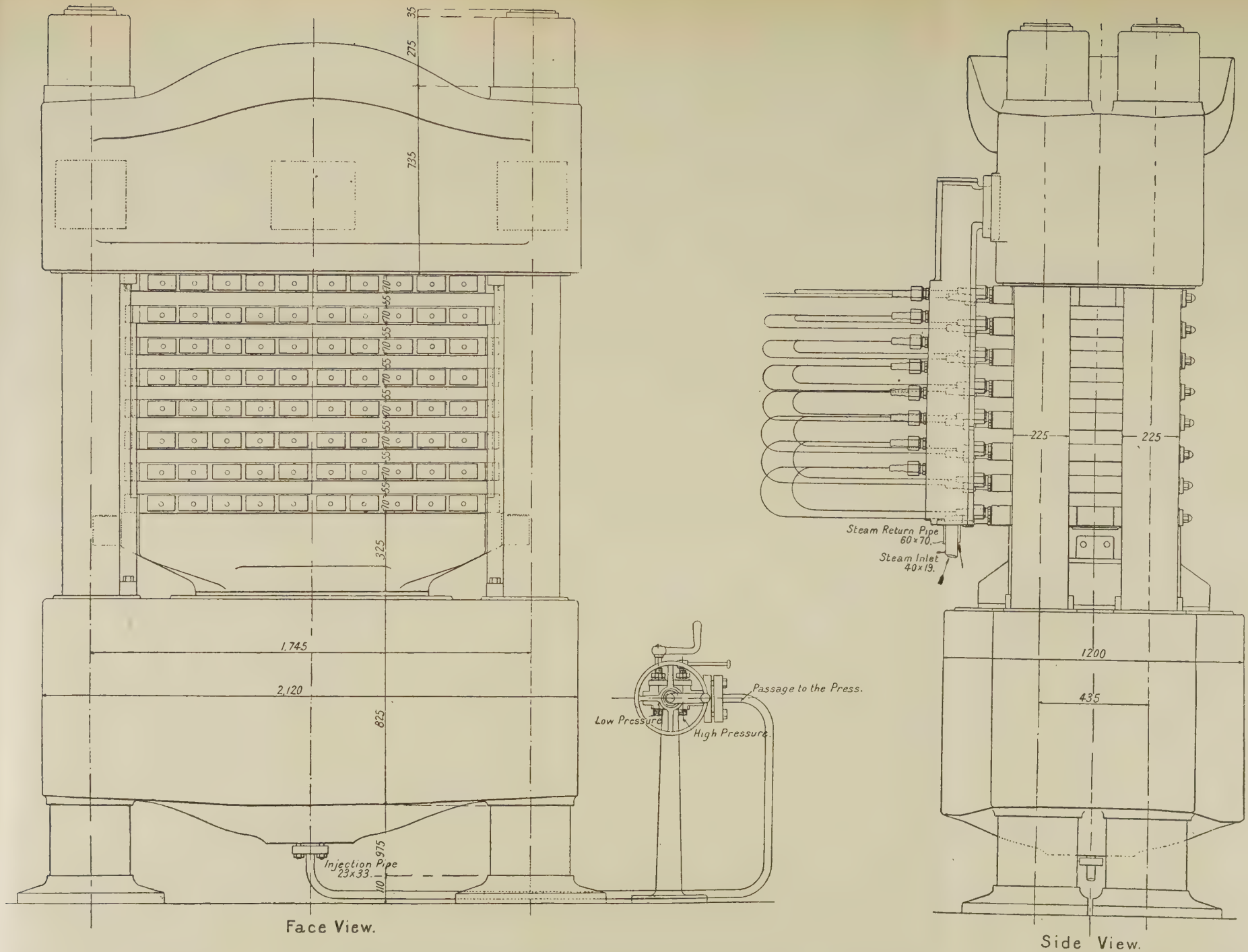
Hand dressing only necessitates a bath having a length about 20 centimetres more than that of the rods, and 1 metre wide by 25 centimetres deep. The dressing table, with iron top, should be 1600 millimetres long and 1000 millimetres wide.

POLISHING.

Sheet polishing. The dressed celluloid sheets are properly rectilinear but their surface is dull, and therefore in many works they are polished. For this purpose a polishing press is used. The latter is identically similar to the dressing press. The plates have the same dimensions and may be heated or cooled by two pipes conveying steam or cold water. The only difference between the presses is in their power.

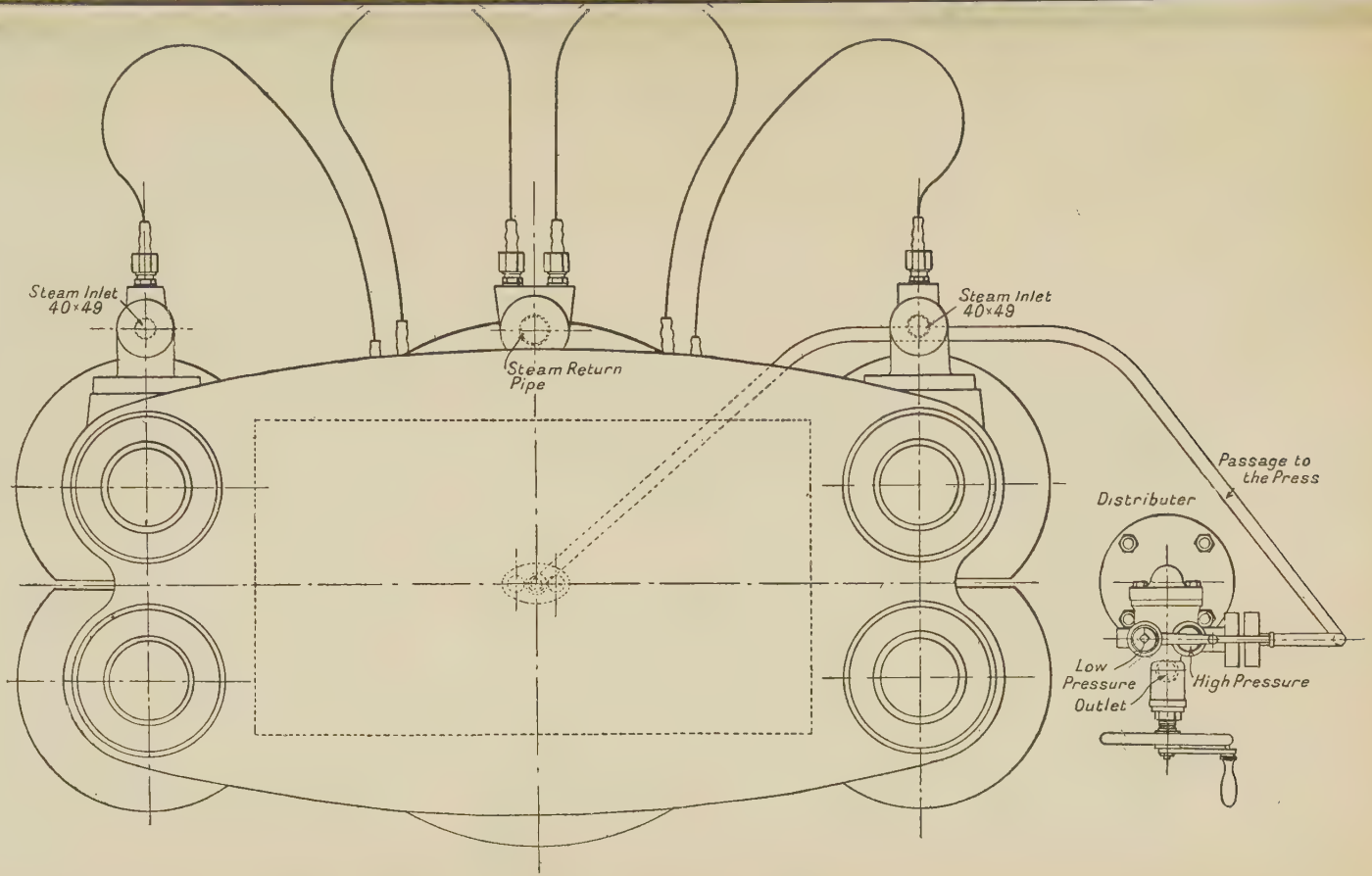
While the dressing press works at 150 kilogrammes pressure per square centimetre, the polishing press requires 500 to 600. Also, while the weight of the dressing press varies from 10,000 to 12,000 kilogrammes, that of the polishing press attains 50 to 60 tons. Plate V. represents a polishing press constructed by Champigneul. These high pressures are obtained by employing the hydraulic multiplier.

The polishing proper. When between two polished plates of rigid metal a celluloid sheet is placed, then pressed and heated, a perfect polish is obtained after cooling. The sheets for polishing are laid one by one or two by two according as to whether both sides are to be polished or only one. The plates



CHAMPIGNEUL'S POLISHING PRESS (ELEVATION) : POWER, 100 TONS : 7 COMPARTMENTS

To face page 130



CHAMPIGNEUL'S POLISHING PRESS (PLAN)

PLATE VI

To face page 130

in ordinary use are of polished brass. Two or three bundles of sheets may be placed between each plate. We recommend the use of polished nickel plates, these having given us excellent results.

The sheets are placed between the press plates with a good thickness of cloth interposed between them. They are pressed at the start at 40 kilogrammes and heated. The press should be heated between 60° and 65° C. Certain works heat even to 85° and 90° C. When this temperature has been attained, the pressure is increased gradually to about 500 kilogrammes. The heating requires about 35 to 40 minutes.

When the celluloid sheets are sufficiently softened they are cooled, the cooling process requiring from 40 to 45 minutes. The total polishing period is about 1½ hours for ordinary thicknesses. When sheets of thicknesses attaining 10 millimetres have to be polished, the pressure is diminished (to about 300 kilogrammes) and the duration of pressing increased (2 hours).

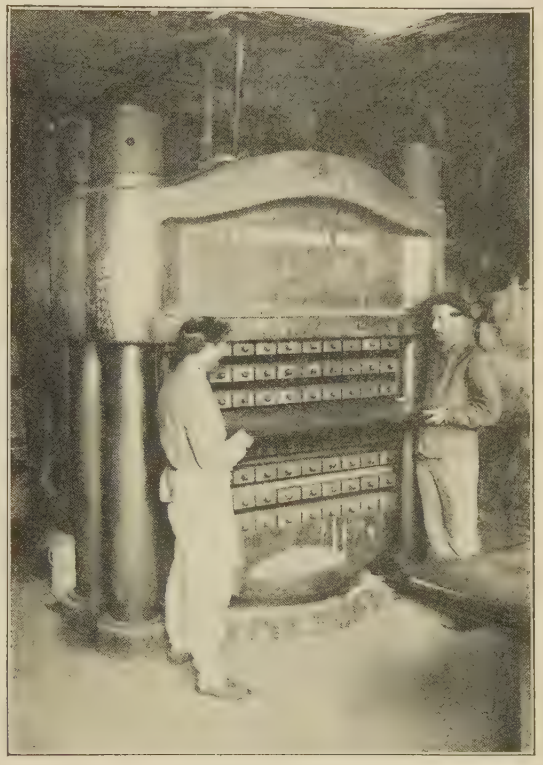


FIG. 69. A Polishing Press.

The polished sheets have their edges trimmed by hand shears before storage.

Installation of the polishing press. The space occupied by this press is about 8 square metres. To the above is adjoined a table which serves for laying the sheets to be polished between copper or nickel plates. In our particular example, a polishing press with 12 plates will amply suffice.

CHAPTER XI

MANUFACTURE OF TUBES. UTILISATION OF WASTE

TUBE MANUFACTURE.

Tube manufacture becomes more and more extensive.

The tubes are made by machines called "stuffings" (in English, Extrusion Machines).

Description of the stuffing. This machine may be either horizontal or vertical, the latter being the type most in use.

The vertical stuffing consists of a frame, the lower part of which carries a box of cast steel, whose walls and centre are hollow. This box is known as the die chamber. In the jacket surrounding this chamber steam or cold water may be passed.

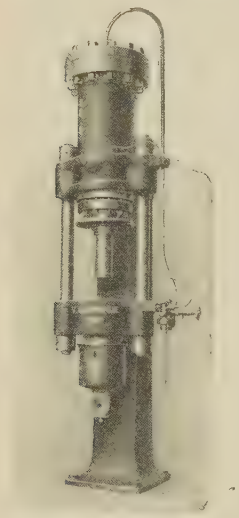


Fig. 70. A Large Champigneul Extrusion Machine (a stuffing).

The lower portion of the die chamber is threaded and contains a steel piece consisting of a sleeve having a central orifice. Upon this piece the die rings are fitted.

Above the spinning chamber is a hydraulic cylinder furnished with a piston whose diameter is within a few millimetres that of the chamber orifice. The hydraulic piston may be lowered or raised at convenience by means of a double distributor which allows water to be compressed on either side.

The action of the stuffing is as follows :

The piston is withdrawn from the die chamber, into which rolls of material are placed.

When the chamber is full, it is heated by means of steam passed into the jacket. At the upper part of the chamber a current of cold water is turned on, the object being to cool the upper material, which would otherwise tend to escape outside under the combined influence of heat and pressure. The pressing may then be undertaken.

For that purpose the piston is gradually lowered by the low pressure, afterwards by 150 kilogrammes pressure.

The material becomes plastic and is forced towards the die ring carrier and past the ball (*le boulet*). This latter is a piece of iron having the form of a shell, whose surface is furnished with ribs against which the celluloid is

compelled to pass and be reduced to small portions. These arrive at the die ring carrier.

The die ring carrier comprises:

(1) A steel bar fixed to the wall of the carrier by a nut. This bar, termed the spindle, is fixed.

(2) A ring, known as the die ring (*filière*), whose position may be regulated by four screws.

The spindle determines the internal space of the tube, the ring the thickness of the walls.

It will easily be gathered that during the extrusion process the ring should be adjusted in such a way that the space between it and the spindle constitutes a perfect annulus. When the die chamber is empty, the arrival of compressed

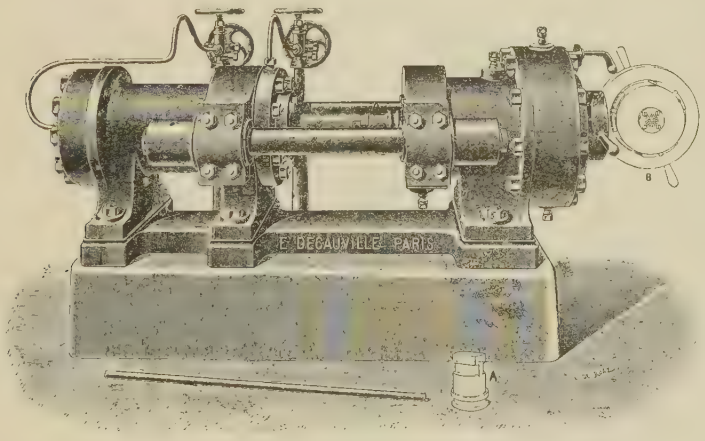


FIG. 71. A Horizontal Stuffing.

water above is suspended and the same turned on below, thus raising the piston.

The die chamber should never be heated higher than 80 degrees. A very convenient temperature is between 68 degrees and 70 degrees.

The rings and spindles vary according to the diameter and thickness to be obtained. By means of striated die rings, tubes with furrowed surface may be made.

Fig. 70 represents a vertical, and Fig. 71 a horizontal stuffing constructed by Decauville.

The management of a stuffing is very delicate and the daily production very variable according to the skill of the operator and the quality of the material.

Rods may also be made by the stuffing, but this process is only used for diameters above 3 centimetres.

Finally, stuffings are also employed for straining the material. Soiled celluloid waste especially is subjected to this operation. In this case a die ring

of 18 to 20 millimetres diameter only is mounted on the ring carrier. In front of the ring is a metallic gauze whose object is to prevent impurities passing. This filter is changed about every hour, or every two hours, according to the cleanliness of the material. The production of filtered threads varies with the hardness and purity of the celluloid. Per hour, from 10 to 12 kilogrammes of celluloid may be filtered.

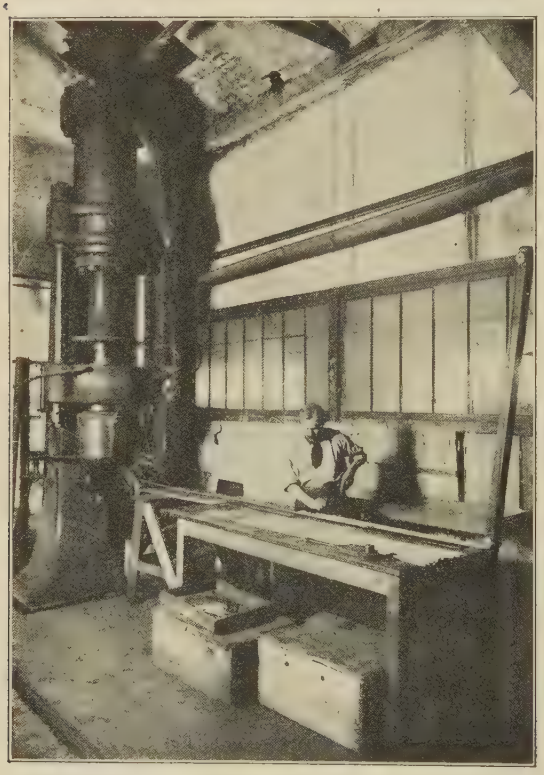


Fig. 72.

THE STUFFING PLANT.

Stuffings are almost always stationed against a wall in the cutting chamber. They occupy about 2 square metres.

As an accessory, a table is necessary upon which to lay the tubes or filtered threads. A plank provided with a system of balance weights permits the continuous working and examination of the tube proceeding from the die ring.

Two stuffings will be necessary for the case we have chosen.

Drying the tubes. For a reason previously given the tubes are placed in a cold drying chamber. Normally 6 to 8 days are required for tube drying, with a maximum of 15 days.

UTILISATION OF THE WASTE.

We have seen in the chapter dealing with the cutting of celluloid, that an appreciable amount of waste is obtained.

From 100 kilogrammes of dry material are obtained :

(1) From sheets, 12 to 15 kilogrammes of waste.

(2) From rods, 80 to 90 kilogrammes of waste.

For the manufacture of 800 kilogrammes of dry material per day of 10 hours into 600 kilogrammes of sheets and 200 of rods, it is necessary to calculate from $\frac{12 \times 600}{100} = 72$ kgr. to $\frac{15 \times 600}{100} = 90$ kgr. of waste from sheets, and

$\frac{80 \times 200}{100}$ = 160 kgr. to $\frac{90 \times 200}{100}$ = 180 kgr. of waste from rods, *i.e.* from 230 to 270 kilogrammes of waste each day.

This waste is clipped, steeped, and mixed with nitrocellulose.

The waste may not be employed in great quantity. That proceeding from rods of imitation tortoise shell may be incorporated anew in a block of imitation shell. Ivory waste is employed for the manufacture of fresh ivories or for simple opaque colours.

Employed alone, 125 to 130 kilogrammes of waste should be equivalent to 100 kilogrammes of new dry material.

The mixtures of nitrocellulose and waste are very variable. Thus 25 to 150 kilogrammes of waste may be added to 100 kilogrammes of pulp : a good average is from 50 to 75 per cent.

We refer the reader to what has been said *à propos* of steeping and rolling waste matters.

The waste for utilisation is stored in tight boxes, which are arranged in well-aired premises destined for such material.

CHAPTER XII

THE GENERAL ORGANISATION OF A CELLULOID WORKS

THE USUAL WORKS' PLANT.

In each separate section of the manufacture we have given information as to the plant required. We shall complete these data by a concise examination of the general installation.

The situation and dimensions of the site occupied. In the first place, a site should be looked for possessing a large supply of available water.

This site should be chosen in a centre possessing the best economic conditions. The ideal is to build a works upon well-consolidated ground, traversed by a river, and in proximity to a railway and a canal. Very few works possess such a situation however. Account must also be taken of the geographical position, which, as far as possible, should be near a large centre whereby all the raw materials may be procured.

Works in general, and especially celluloid works, are being installed more and more in mountainous districts where waterfalls exist. This idea is certainly a good one, but the question must be studied in all its bearings, since there are often fluctuations in the strength and duration of certain falls. We are able to mention a certain celluloid firm whose work is often impeded by the failure of the hydraulic power.

THE MOTIVE POWER NECESSARY.

We shall consider in detail the motive power necessary for a plant unwinding 500 kilogrammes of paper in 10 hours.

High-pressure pump		8 h.p.
Low-pressure pump		5 ,,
Nitration	Unwinding	2 ,,
	2 centrifugalisers	12 ,,
Bleaching	1 pile	8 ,,
	1 pump	3 ,,
	2 hydro-extractors	10 ,,
Drying and grinding	2 mills	3 ,,
	1 grinder	1 ,,
Rolling	1 kneader	6 ,,
	5 rolling mills	50 ,,
Cutting	2 cutting machines	12 ,,
We, therefore, have a total of		120 h.p.

By also reckoning the water feed-pipe, the dynamo and the power necessary in the mechanics' workshop, we arrive at a total of 150 h.p.

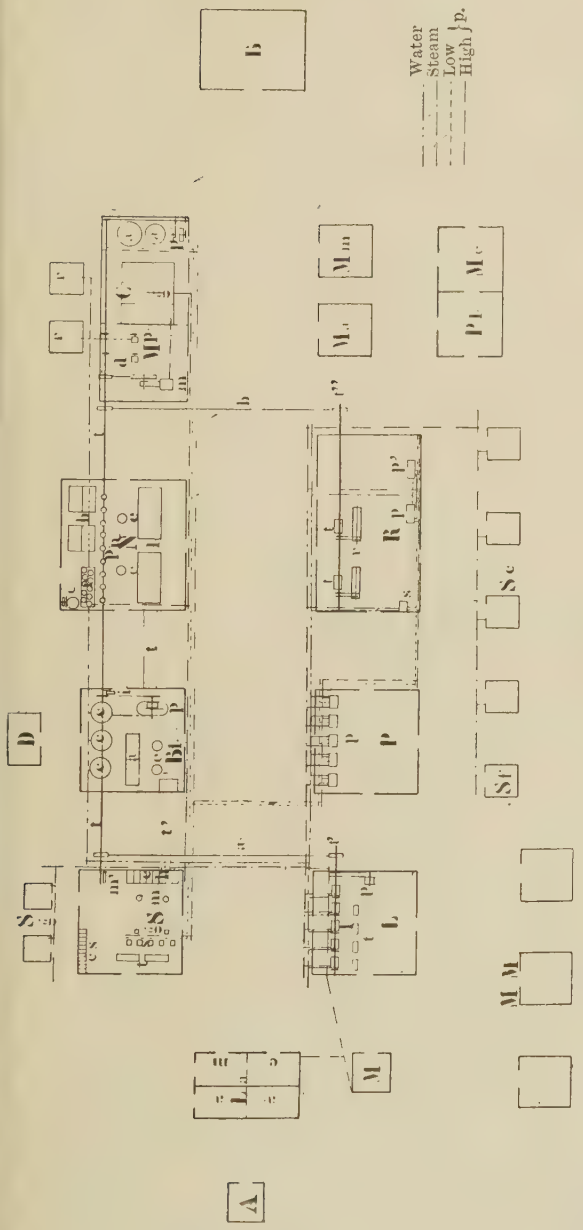


FIG. 73.

B. Offices.

C. Boilers.

- g Generators
- a Low-pressure accumulators
- a' High-pressure accumulators
- p Pumps at high and low pressure
- r Water reservoirs

M. Engine Room

- m Steam engine
- p Water feed pump
- d Dynamo

N. Nitration Chamber

- pn Nitration pots
- ee Centrifugalisers
- r Pots for preparing the acid mixtures
- b Acid tanks
- c Air compressor
- l Baths for washing the nitrated paper
- t Transporter for the nitrated paper

Bl. Bleaching

- p Hollander pile
- i Pulp pump
- c Bleaching vats
- d Draining vats
- e Hydro-extractors
- t' Transporter for the bleached pulp

S. Cake Drying

- ch Cases for moist pulp
- m Mills
- g Cake presses
- s Cake drying press
- t Work tables
- cs Cases for dry pulp
- m' Mill for dry pulp
- Sg Drying plant for the drying cloths

L. Rolling Machines

- l Rolling machines
- t Manipulation tables
- p Kneader

P. Block Presses

- p Presses

R. Cutting Room

- r Planing machines
- t Tables
- s Stuffing
- p Dressing press
- p' Polishing press
- Sc Hot drying chambers for sheets
- Sf Cold drying chamber for rods and tubes
- M Solvent preparation room

La. Laboratory

- c Colour preparation
- m Preparation of alcohol mixtures
- a Analytical rooms
- A Depôt for alcohol and other solvents
- D Depôt for celluloid waste
- MM Celluloid depôts
- Ma Works' store
- Mm Celluloid delivery warehouse
- Pl, Mc Workshops for plumbers, mechanics, &c.

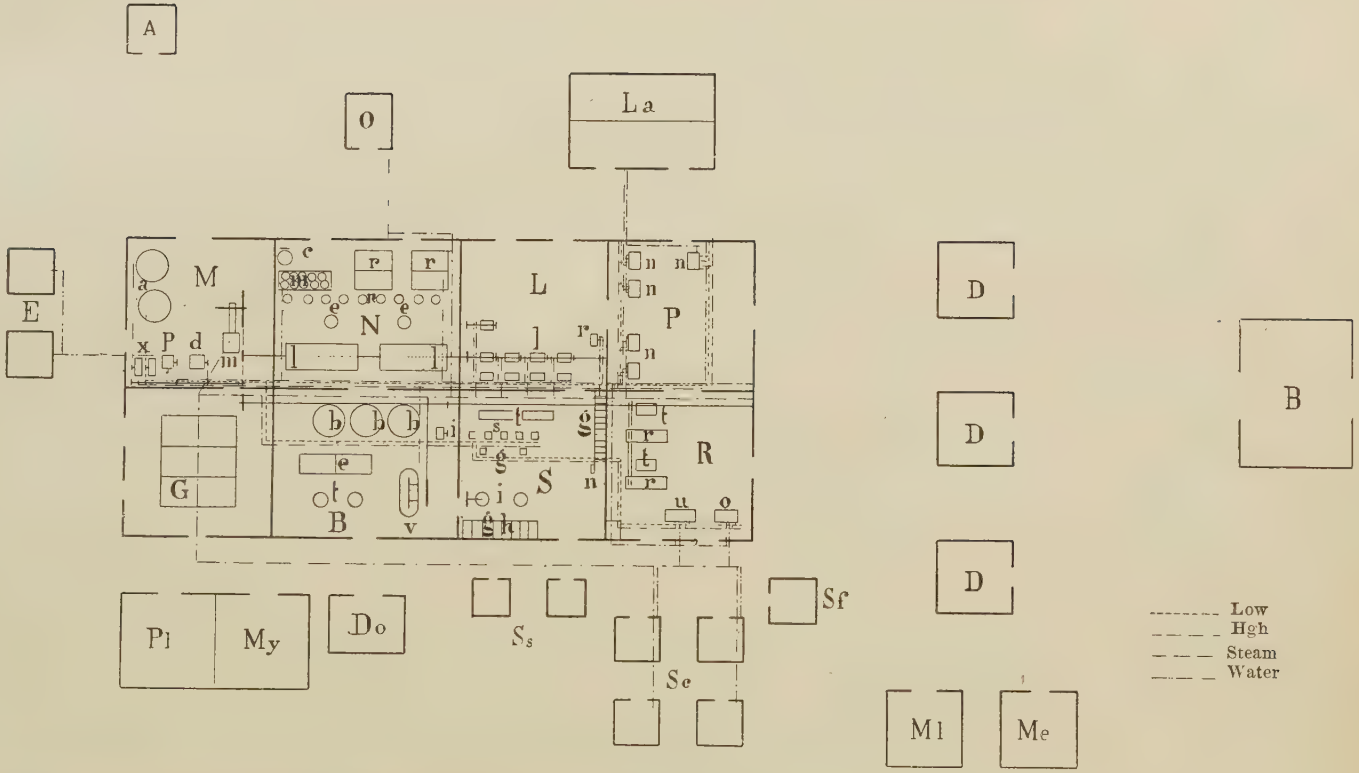


Fig. 74.

G. Boiler house

M
- **m** Motor
- **d** Dynamo
- **p** Water pump feeding the works
- **a** High and low pressure accumulators
- **x** High and low pressure pumps

E Water reservoirs

N. Nitration
- **c** Air compressor
- **m** Pots for preparation of acid mixtures
- **rr** Acid tanks
- **n** Nitration pots
- **ee** Centrifugalisers
- **ll** Washing vats for nitrated paper

B. Bleaching
- **v** Hollander pile
- **i** Pulp pump
- **bbb** Bleaching vats
- **e** Drainers for moist pulp
- **t** Pulp hydro-extractors

S. Drying of the pulp
- **gh** Chests for the moist pulp
- **i** Mills
- **g** Cake presses
- **s** Cake drying presses
- **t** Work-table
- **gs** Chests for the dry cakes
- **n** Cake grinder

L. Rolling
- **ss** Chambers for drying cloths
- **j** Rolling mills
- **r** Kneader
- **t** Work-tables

P. Pressing
- **n** Presses

R. Cutting
- **rı** Planing machines
- **u** Dressing press
- **o** Polishing press. **s** Stuffing
- **t** Work-tables

Sc Hot drying chambers for material
Sj Cold drying chambers for tubes and rods
D Depôts for manufactured celluloid
Do Waste depôts
Ml Works' store
Me Delivery store
B Offices
La Laboratories
O Preparation of solvents
A Alcohol store
Pl Plumbers' shop
My Mechanics' shop

SITUATION OF THE BUILDINGS.

Two types of works' plant may be considered:

(1) The type with detached buildings.

(2) That with connected buildings.

Type with isolated workshops. The object of this mode of installation is for the prevention of fire dangers. The figure appended is a correct survey of this type of plant.

On page 137 are the installation details.

Upon this plan may be noticed an underground power transmission *t*, which proceeding from the engine room *M*, terminates at the cake drying workshop *S*. Two gearings at *b* and *a* drive the lines *t''* and *t'*. The transmission line *f''* drives the planing machines, and the line *t'* works the rollers and kneader.

The two rows of buildings are separated by 20 metres, each building is separated from its neighbour by 12 metres. This type of plant occupies a large space, and in many cases of fire, the buildings, in spite of their detachment, have easily been the prey of the flames.

Accordingly the present tendency is to collect the buildings of a celluloid works together.

Figure 71 gives the plan of such an assembled celluloid works, the plant of which is similar to that existing in the installation of the figure.

The installation details will be found on the previous page (139).

THE STORAGE OF CELLULOID.

There is nothing very special about the storage of celluloid. We need only say that the stores should be detached and well ventilated. The material is placed in chests which should be guaranteed dust proof as far as possible.

In general, the storing of celluloid for long periods should be avoided.

CHAPTER XIII

ANALYSES REQUIRED IN A CELLULOID WORKS

To obtain a sulphonitric mixture of given composition by means of acid mixtures. Possessing a sulphonitric mixture having the following percentage composition :

HNO_3	12·20
H_2SO_4	66·90
H_2O	20·90

what quantity of the following mixture :

HNO_3	15·00
H_2SO_4	76·20
H_2O	8·20

should be added to bring the composition to :

HNO_3	13·21
H_2SO_4	69·69
H_2O	17·10

Let us add 10 kilogrammes of the disposable mixture to the mixture for use ; we shall obtain :

HNO_3	H_2SO_4	H_2O
12·20	66·90	20 90
1·50	7·68	0·82
13·70	74·58	21·72

This for : 100 kilos.
10 „
110 „

Therefore for 100 kilogrammes :

HNO_3	12·45
H_2SO_4	67·80
H_2O	19·74

It will be seen that 10 kilogrammes of the sulphonitric mixture do not suffice.

Let us add 30 kilogrammes of sulphonitric mixture, we shall obtain :

HNO_3	H_2SO_4	H_2O	Weight.
12·20	66·90	20·90	100 k.
4·50	23·04	2·46	30
16·70	89·94	23·36	130 k.

Therefore for 100 kilogrammes :

HNO_3	12·84
H_2SO_4	69·18
H_2O	17·72

We have not yet obtained the percentage content required ; let us add 40 kilogrammes of mixture :

HNO_3	H_2SO_4	H_2O	Weight.
12·20	66·90	20·90	100 k.
6·00	30·72	3·28	40
18·20	97·62	24·18	140 k.

The percentage composition is :

HNO_3	13·00
H_2SO_4	69·72
H_2O	17·27

This composition is therefore the best.

To obtain a given sulphonitric mixture by means of fresh acids. Suppose that a sulphonitric mixture is required having the following percentage composition :

HNO_3	13 50
H_2SO_4	68·20
H_2O	18·30

The degree Baumé of the nitric and sulphuric acids to be employed is first taken.

Then from the Tables the nitric acid content is found corresponding to the degree Baumé and the temperature of the acid.

Suppose that we have

HNO_3 at 15°	40·5°
H_2SO_4 at 15°	65·6°

Therefore per 100, our acids contain in monohydrate :

HNO_3	92·72
H_2SO_4	63·23

Accordingly our mixture should contain per 100 :

$$HNO_3 = \frac{13{\cdot}5 \times 100}{62{\cdot}23} = 21{\cdot}35 \text{ gr.}$$

$$H_2SO_4 = \frac{68{\cdot}2 \times 100}{92{\cdot}73} = 73{\cdot}55 \text{ gr.}$$

$$H_2O = 100 - (HNO_3 + H_2SO_4) \text{ or}$$

$$100 \text{ gr.} - (21{\cdot}35 + 73{\cdot}55) = 5{\cdot}10 \text{ gr.}$$

Analysis of a sulphonitric mixture. Ordinarily a sulphonitric mixture contains:

(1) Nitric acid;
(2) Sulphuric acid;
(3) Water.

We commence by taking a known weight of the acid mixture, and placing it in a measured dropping-flask. This done, a small quantity of the sulphonitric mixture to be analysed is poured into the funnel of a nitrometer. (Fig. 75.)

This nitrometer consists of two tubes *a* and *b* connected together by a rubber tube. The tube *a* has a funnel at its upper extremity provided with a 3-way cock; immediately below this cock is a glass bulb whose capacity is usually 100 cubic centimetres.

From this glass bulb the tube *a* is graduated into 100 or 150 divisions corresponding to a cubic centimetre. Each cubic centimetre is subdivided into tenths. The tube *b* is open at its upper extremity.

Mercury is poured into the tube *a*; the level of the latter should reach the top of the glass bulb. By means of the rubber tubing the tube *b* may be raised or lowered.

The use of the nitrometer is based upon the evolution of gaseous nitric oxide formed when nitric acid comes into contact with mercury.

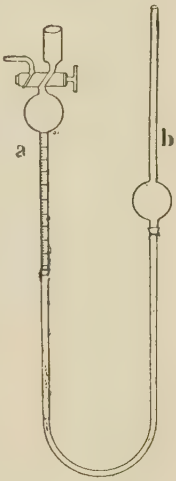


FIG. 75. The Nitrometer.

The sulphonitric acid is poured into the funnel after completely expelling the air from the glass bulb.

The sulphonitric acid is made to pass into the latter by carefully manipulating the cock which communicates between funnel and glass bulb.

The funnel is twice rinsed out with about 10 cc. sulphuric acid.

Entrance of air into the apparatus should be entirely avoided.

The tube *a* is then taken and vigorously shaken many times; this causes an evolution of nitric oxide which gradually displaces the mercury, this being driven back into the tube. When the evolution of gas has entirely ceased, an interval of 10 minutes is allowed before reading the volume of the gas.

For the latter operation, the levels are adjusted to the same in both tubes; the tube *b* should be raised so that the mercury level in *b* may be higher by $\frac{1}{7}$ of the height of the mercury in *a* (because of the difference in density between mercury and acid).

The equality of level is checked by allowing a drop of sulphuric acid to pass into the funnel. This drop should remain in equilibrium when the cock connecting the bulb is opened. The tube *b* is raised or lowered according as the drop tends to recede from the cock or enter it. When the pressure is the same in both tubes, the volume of the gaseous product is taken. This

volume is corrected for temperature and pressure according to the following formula:

$$A\,a = \frac{AP}{760\,(1 + \Delta\,t)}$$

A = Volume read (in cubic centimetres).
P = Barometric pressure.
760 = Normal barometric pressure.
Δ = a coefficient whose value is 0·003665.
t = Temperature at which the observation is made.
Aa = Corrected volume.

On the opposite page are the values of $760\,(1 + \Delta\,t)$ for temperatures varying between 10° and 30° C.

Let p = the weight of sulphonitric mixture poured into the nitrometer.

The following formula may be applied:

$$\frac{AP \times 100 \times 0{\cdot}28202}{760\,(1 + \Delta\,t \times p)}$$

0·28202 gr. is the quantity of nitrogen corresponding to 1 cc. NO.

Let us take for example the following data:

A = 78 cc.
P = 770
p = 1·50 gr.
t = 24° C.

According to the above Table the value of $760\,(1 + \Delta\,t)$ at 24° = 826·8496.

$$\frac{78 \times 770 \times 100 \times 0{\cdot}28202}{826{\cdot}8496 \times 1{\cdot}5} = 13{\cdot}77$$

Our sulphonitric mixture therefore contains 13·77% of HNO_3.

We next consider the sulphuric acid content by weighing a fresh portion of the sulphonitric mixture and neutralising by means of a standard soda solution. Knowing the H_2SO_4 content, the water in the mixture is obtained by difference:

$$100 - (HNO_3 + H_2SO_4) = H_2O.$$

By means of the nitrometer the nitrogen content of nitrocellulose may in like manner be obtained.

An alternative method. Frequently, the following analytical method may be employed for a sulphonitric mixture. The nitric acid is separated from the sulphuric by forming an easy compound with it, *e.g.*, by allowing it to nitrate benzene. The sulphuric acid which remains after separating the nitrobenzene is determined volumetrically. In practice, the total acidity is first estimated in 50 grammes of mixture, which is diluted to 500 cc., and then 25 cc. at a time titrated with soda.

The nitrous acid is next determined by potassium permanganate. Finally,

Gaseous Volume Corrections.

t	$760\ (1+\Delta t)$	t	$760\ (1+\Delta t)$	t	$760\ (1+\Delta t)$	t	$760\ (1+\Delta t)$
° C.		° C.		° C.		° C.	
10·0	787·8540	15·1	802·0595	20·1	815·9865	25·1	829·9135
1	788·1325	2	802·3381	2	816·2651	2	830·1921
2	788·4111	3	802·6166	3	816·5436	3	830·4706
3	788·6896	4	802·8952	4	816·8222	4	830·7492
4	788·9682	5	803·1737	5	817·1007	5	831·0277
5	789·2467	6	803·4522	6	817·3792	6	831·3062
6	789·5252	7	803·7308	7	817·6578	7	831·5848
7	789·8038	8	804·0093	8	817·9363	8	831·8633
8	789·9823	9	804·2879	9	818·2149	9	832·1419
9	790·3609	16·0	804·5664	21·0	818·4934	26·0	832·4204
11·0	790·6394	1	804·8449	1	818·7719	1	832·6989
1	790·9179	2	805·1235	2	819·0505	2	832·9775
2	791·1965	3	805·4020	3	819·3290	3	833·2560
3	791·4750	4	805·6806	4	819·6076	4	833·5346
4	791·7536	5	805·9591	5	819·8861	5	833·8131
5	792·0321	6	806·2376	6	820·1646	6	834·0916
6	792·3106	7	806·5162	7	820·4432	7	634·3702
7	792·5896	8	806·7947	8	820·7217	8	834·6487
8	792·8677	9	807·0733	9	821·0003	9	834·9273
9	793·1463	17·0	807·3518	22·0	821·2788	27·0	834·2058
12·0	793·4248	1	807·6303	1	821·5573	1	835·4843
1	793·7033	2	807·9089	2	821·8859	2	835·7629
2	793·9819	3	808·1874	3	822·1114	3	836·0414
3	794·2604	4	808·4660	4	822·3930	4	836·3200
4	794·5390	5	808 7445	5	822·6715	5	836·5985
5	794·8175	6	809·0230	6	822·9500	6	836·8770
6	795·0960	7	809·3016	7	823·2286	7	837·1556
7	795·3746	8	809·5801	8	823·5071	8	837·4341
8	795 6531	9	809·8587	9	823·7857	9	837·7127
9	795·9317	18·0	810·1372	23·0	824·0642	28·0	837·9912
13·0	796·2102	1	810·4175	1	824·3427	1	838·2697
1	796·4887	2	810·6943	2	824·6213	2	838·5483
2	796·7673	3	810 9728	3	824·8998	3	838·8268
3	797·0458	4	811·2514	4	825·1784	4	839·1054
4	797·3244	5	811·5299	5	825·4569	5	839·3839
5	797·6029	6	811·8084	6	825·7354	6	839·6624
6	797·8814	7	812·0870	7	826·0140	7	839 9410
7	798·1600	8	812·3655	8	826·2925	8	84)·2195
8	798·4385	9	812·6441	9	826·5711	9	840·4981
9	798·7171	19·0	812·9226	24·0	826·8496	29·0	840·7766
14·0	798·9956	1	813·2011	1	827·1281	1	841·0551
1	799·2741	2	813·4797	2	827 4067	2	841·3337
2	799·5527	3	813·7582	3	827·6852	3	841·6122
3	799·8312	4	814·0368	4	827·9638	4	841·8908
4	800·1098	5	814·3153	5	828·2423	5	842·1693
5	800·3883	6	814·5938	6	828·5208	6	842·4478
6	800·6668	7	814·8724	7	82 ·7994	7	842·7264
7	800·9454	8	815 1500	8	829·0779	8	843·0049
8	801·2239	9	815·4925	9	829·3565	9	843·2835
9	801·5025	20·0	815·7080	25 0	829·6350	30·0	843·5620
15·0	801·7810						

the sulphuric acid is estimated by weighing 50 grammes of the mixture and adding to it 50 cc. of benzene. The mixture is gently heated to start the re-action. At the end of about a quarter of an hour, when the re-action has

terminated, a fresh 10 cc. of benzene is added with shaking. The mixture is poured into a separate funnel containing 300 cc. water. The nitrobenzene is then separated and washed once or twice. The waters from the separation and washings are run into a 500 cc. flask and made up to bulk. The acidity is then estimated in 25 cc. after being assured by tests that no nitric acid is present.

Estimation of the nitrogen in nitrocellulose. A known weight of nitrocellulose (about 0·5 gr.) is taken, placed in a well-stoppered flask and acted upon by sulphuric acid of 60° Baumé. The nitrocellulose is allowed to dissolve in the H_2SO_4, and when complete solution has taken place it is poured into the nitrometer, care being taken to thoroughly wash the flask and funnel. The operation is then conducted as for the estimation of HNO_3 in sulphonitric mixtures. The formula employed is the same except that 1 cc. NO corresponds to 0·6267 N.

The following Table gives the weights in milligrammes of the gases N, NO, NO_2 and HNO_3 corresponding to the volume of nitric oxide NO measured in cubic centimetres at 0° C. and 760 mm. pressure.

Weight in Milligrammes.

Number of cc. of NO	N	NO	NO_2	HNO_3
1	0·627	1·343	2·060	2·820
2	1·254	2·686	4·120	5·640
3	1·881	4·029	6·180	8·460
4	2·508	5·372	8·240	11·280
5	3·135	6·715	10·300	14·100
6	3·762	8·058	12·360	16·920
7	4·389	9·401	14·420	19·740
8	5·016	10·744	16·480	22·560
9	5·643	12·087	18·540	25·380

Analysis of camphor. The camphor analysis should include:

(1) The colour of its solution.
(2) The proportion of its insoluble matter.
(3) The contained moisture.

The solution should have no colour and be quite clear.

As for insoluble matter it should not exceed 0·50 per cent. In the case of Formosa camphor, the amount of insoluble matter rarely exceeds 0·20 per cent.

The moisture contained in camphor varies between wide limits.

Formosa camphors do not usually contain more than 1 per cent. of moisture.

Estimation of moisture. The drying may not be carried out in vacuo

or over sulphuric acid, because of the tendency of camphor to volatilise. The most usual procedure is by compression.

A weight x of camphor is taken, placed on sheets of filter paper, and compressed by the hydraulic press. The water squeezed out is absorbed by the paper. On weighing, the moisture absorbed by the paper is obtained by difference.

This method is not very accurate, since besides the water which impregnates the paper there is the oil contained in the camphor which also passes out.

The following procedure may be followed :

100 grammes of the camphor to be analysed are taken and placed in a test-tube; this is triturated with 100 cc. of a standard soda solution. A short interval for contact is allowed, then the solution is filtered and 50 cc. of the filtrate neutralised with standard sulphuric acid solution. The water contained in the camphor is thus obtained.

Let us take the following example:

$$100 \text{ cc. } NaOH = 100{\cdot}5 \text{ cc. } H_2SO_4$$

Therefore, for neutralising 50 cc. of soda which has washed the camphor, 48·3 cc. of H_2SO_4 are necessary.

Hence, the percentage moisture is:

$$\frac{50 \times 100{\cdot}5}{48{\cdot}3} - 100 = 4{\cdot}02 \text{ per cent.}$$

ANALYSIS OF CELLULOID.

Celluloid analysis is very difficult. Generally a qualitative analysis is made, since a complete quantitative analysis is impossible with the actual means at our disposal.

When celluloid is manufactured exclusively with camphor a fairly exact analysis may be made, but when manol, acetanilide celludol, &c., are added to the camphor, the analysis cannot be very accurate.

The procedure of a complete analysis. 50 grammes of the celluloid for analysis are finely powdered and placed in a glass thimble, which is put into a large Soxhlet apparatus mounted upon a round-bottomed flask containing ether. This is gently heated and extracted four or five times; the camphor dissolves, and it only remains to evaporate the ether slowly and thus obtain the camphor and its substitutes.

On drying by pressure the camphor and its included substitutes are obtained. The residue may not be dried in vacuo because of the great facility with which camphor volatilises. Drying over sulphuric acid also occasions loss, the acid absorbing camphor. This loss, it is true, may be diminished by saturating the acid with camphor.

This method may be modified by placing the celluloid powder in a round-bottomed flask containing distilled water to which 25 per cent. of caustic soda has been added. A condenser is attached to the flask terminating in a strongly

cooled receiver. Steam then carries away the camphor, which is recovered in the condenser and receiver.

The refractometer method. M. Utz, in the *Journal de Pharmacie et de Chimie*, describes the following procedure :

"After extracting the powdered celluloid in a Soxhlet by means of ether or petrol, the solution is evaporated ; the camphor obtained is dissolved in methyl alcohol; the solution made to a known bulk and the deviation taken by the Immersion Refractometer of Zeiss. Let N be this deviation.

In addition the deviation of the methyl alcohol employed is taken ; let it be *n*.

The difference N – *n* gives for the following values :

1·0	0·250	of camphor in	100 cubic centimetres
2·0	0·500	,,	,,
3·0	0·750	,,	,,
4·0	1·000	,,	,,
8·0	2·000	,,	,,
12·0	3·190	,,	,,
14·0	3·810	,,	,,
16·0	4·410	,,	,,
18·0	5·000	,,	,,

The author has found in parings from various objects from 20·15 to 28 per cent. of camphor.

We give below a description of Zeiss' refractometer and the mode of employment.

THE IMMERSION REFRACTOMETER OF ZEISS.

The refractometer serves to measure the refractive indices of aqueous, alcohol, or dilute ether solutions. In practice the scale readings of the apparatus take the place of the indices, but may be transformed, if necessary, into the indices proper by means of a Table.

The method of measurement is based on the observation of the limit of total reflexion by a telescope.

The apparatus (Fig. 76) consists of :

(1) A glass prism *P* having a refracting angle of 63 degrees.

(3) A telescope with objective *O* and eyepiece *Oc* furnished with a scale *Sc* and micrometer screw *Z*. This telescope is rigidly attached to the prism.

(3) A compensator *A* interposed between the prism *P* and the telescope objective *O*. This compensator turns about the axis of the telescope. Rotation is brought about by the ring *R*.

On account of the dispersion differences between glass and liquid, the line of separation between the clear and dark zones of the field of view of the eyepiece is usually tinted, and does not permit of accurate observations. By turning

the compensator with the ring R, the line of separation is rendered distinct and colourless.

It is the position of this line of separation or limit on the eyepiece scale, which gives the refraction index of the substance examined, after consulting the Table giving the correspondence between the indices n_D and the scale divisions.

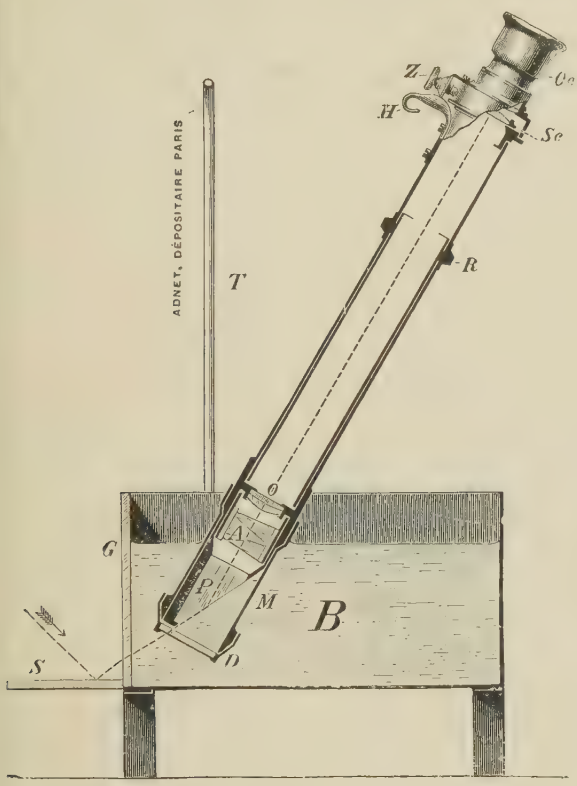


FIG. 76. Section of Zeiss' Immersion Refractometer.

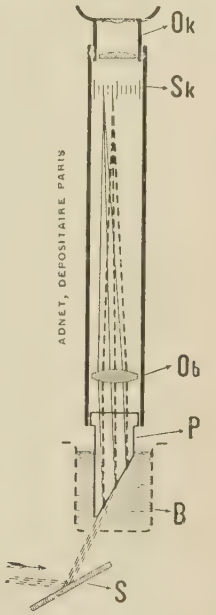


FIG. 77. The Principle of the Immersion Refractometer.

Method of measurement. The reading is made direct, the whole divisions being noted. The micrometer screw serves to determine the tenths. By turning the head Z the scale is displaced until the division noted falls exactly on the zone limit. The screw scale then indicates the tenths to be added to the whole numbers.

This process admits of absolute accuracy. When the readings are carefully taken they differ among themselves by less than 0·1 of a division, either on one side or the other, which corresponds to an average of 3·7 units of the 5th decimal place of n_D. Great accuracy is therefore obtained.

The solutions are examined at the normal temperature of 17·5° C. This temperature has been adopted in preference to 15° C. because it is easier to

Table for transformation of the immersion refractometer scale divisions into refractive indices n_D and vice versa.

Division	$n_D = 1{\cdot}3$
−5	25 39
−4	25 78
−3	26 18
−2	26 57
−1	26 96
0	27 36
1	27 75
2	28 14
3	28 54
4	28 93
5	29 32
6	29 71
7	30 10
8	30 49
9	30 87
10	31 26
11	31 65
12	32 04
13	32 42
14	32 81
15	33 20
16	33 58
17	33 97
18	34 35
19	34 74
20	35 13
21	35 51
22	35 90
23	36 28
24	36 67
25	37 05
26	37 43
27	37 81
28	38 20
29	38 58
30	38 96
31	39 34
32	39 72
33	40 10
34	40 48
35	40 86
36	41 24
37	41 62
38	41 99
39	42 37
40	42 75
41	43 13
42	43 50
43	43 88
44	44 26
45	44 63
46	45 00
47	45 37
48	45 75
49	46 12
50	46 50

40	
1	4·0
2	8·0
3	12·0
4	16·0
5	20·0
6	24·0
7	28·0
8	32·0
9	36·0

39	
1	3·9
2	7·8
3	11·7
4	15·6
5	19·5
6	23·4
7	27·3
8	31·2
9	35·1

38	
1	3·8
2	7·6
3	11·4
4	15·2
5	19·0
6	22·8
7	26·6
8	30·4
9	34·2

Division	$n_D = 1{\cdot}3$
50	46 50
51	46 87
52	47 24
53	47 61
54	47 98
55	48 36
56	48 73
57	49 10
58	49 47
59	49 84
60	50 21
61	50 58
62	50 95
63	51 32
64	51 69
65	52 05
66	52 42
67	52 79
68	53 16
69	53 52
70	53 88
71	54 25
72	54 61
73	54 97
74	55 33
75	55 69
76	56 06
77	56 42
78	56 78
79	57 14
80	57 50
81	57 86
82	58 22
83	58 58
84	58 94
85	59 30
86	59 66
87	60 02
88	60 38
89	60 74
90	61 09
91	61 45
92	61 81
93	62 17
94	62 52
95	62 87
96	63 23
97	63 59
98	63 94
99	64 29
100	64 64
101	65 00
102	65 35
103	65 70
104	66 05
105	66 40

37	
1	3·7
2	7·4
3	11·1
4	14·8
5	18·5
6	22·2
7	25·9
8	29·6
9	33·3

36	
1	3·6
2	7·2
3	10·8
4	14·4
5	18·0
6	21·6
7	25·2
8	28·8
9	32·4

35	
1	3·5
2	7·0
3	10·5
4	14·0
5	17·5
6	21·0
7	24·5
8	28·0
9	31·5

EXAMPLE. Let us suppose that for methyl alcohol the limit is at 8·7; the index will be $n_D = 1{\cdot}33049 + 0{\cdot}7 \times 33$ units of the fifth decimal figure. Table 38 of proportional parts gives $0{\cdot}7 \times 38 = 26{\cdot}6$. Therefore $n_D = 1{\cdot}33049 + 0{\cdot}0002 = 1{\cdot}33076$.

maintain the surrounding room temperature at 17·5° than at 15° C. In consequence the refractometer is regulated to indicate the standard value, *i.e.* 15·0 divisions for distilled water at the temperature 17·5° C.

For measurement the solution to be examined must be placed in an air-tight vessel, or better in a filter vessel contained in a bath.

The lower extremity of the refractometer is immersed in one of the filter vessels contained in the first row.

In the Figure below, the base of the bath *A* is formed of a glass plate, below

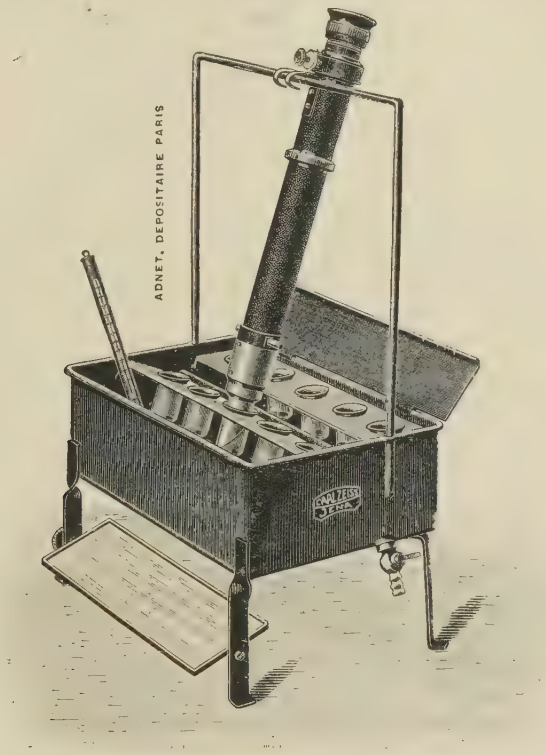


Fig. 78. The Refractometer arranged for an Experiment.

which is a rectangular mirror for reflecting sunlight into the liquid contained in the filter vessels and thence into the refractometer.

The latter is held by two hooks to a vertical frame. By looking through the eyepiece a dark and a clear zone are distinguished, whose line of separation cuts the graduated scale. (Fig. 79.)

The adjustment of the apparatus. Before making measurements it is necessary to adjust the apparatus, which is made as follows: The bath *A* is placed so that the mirror may be turned towards the sky. The vessel is filled a little more than half with the liquid to be examined, and another filled with distilled water is placed in one of the holes of a stand above the mirror. The

refractometer is suspended from the vertical frame by hooks and the prism immersed in the distilled water.

The apparatus is then allowed to stand for about 10 minutes, to allow for temperature equalisation. When the distilled water has assumed the same

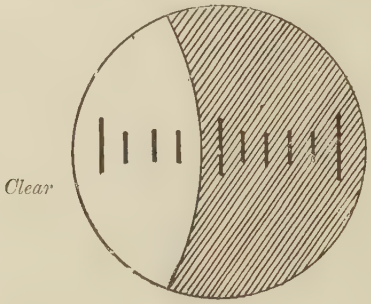


Fig. 79.

temperature as the bath, the eyepiece is adjusted to the mark by turning the milled ring which surrounds its rim. The numbers and scale divisions should then be very distinct. The mirror is then turned until the gleam of the sky is seen to traverse the filter vessels. The upper part of the field of view, from 0 to about 15 appears clear, and is separated from the dark lower portion by a distinct line of separation, if the graduation of the compensator ring is at 5.

The reading of the whole divisions plus the tenths is then taken as described previously, at the same time noting the temperature of the distilled water.

It is hardly necessary to maintain the water temperature at 17·5° C. for this verification. It suffices to see that the readings agree with the following in regard to temperatures :

Temperatures	Divisions	Temperatures	Divisions
10° C.	16·3	20° C.	14·5
11	16·15	21	14·25
12	16·0	22	14·0
13	15·85	23	13·75
14	15·7	24	13·5
15	15·5	25	13·25
16	15.3	26	13·0
17	15·1	27	12·7
17·5	15·0	28	12·4
18	14·9	29	12·1
19	14·7	30	11·8

Several readings are taken. If the mean of these readings differs by more than 0·1 of a division from a value on the preceding Table we proceed as follows : the micrometer disc is adjusted to 10 and the regulating bars, to be found in the

instrument case, are introduced into one of the four holes of the nickel-plated screw cap situated on its inner side. The screw is turned in the direction of the small numbers of the disc, so as to loosen the milled nut which secures it. The temperature of the water is noted and the corresponding normal value deduced from the Table.

By operating on the regulating bar, the line of zone separation is taken exactly to this division. The disc of the micrometer having been loosened is turned

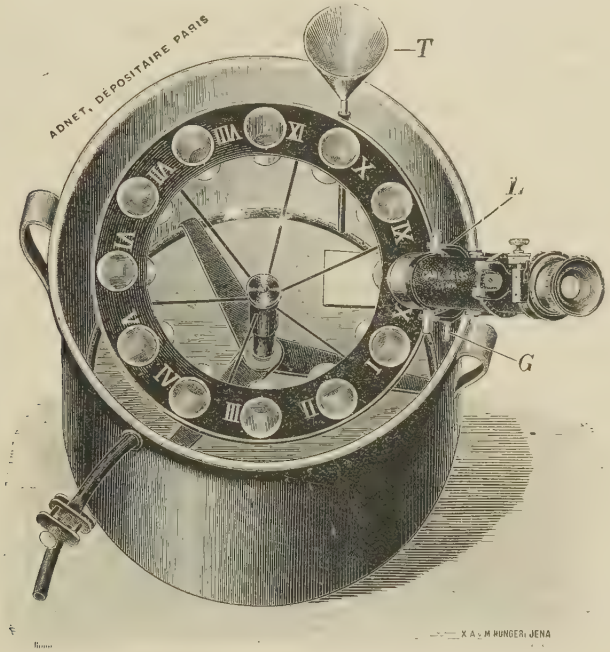


FIG. 80. An Adjustable Bath seen from above.

until its index indicates the tenths, then maintaining the disc the nut is tightened again. This fresh adjustment is checked by a series of readings.

It is necessary that the solution temperature should be constant and the same as that of the bath. This result may be obtained, for experiments of short duration, by allowing water contained in a tank at the surrounding temperature to flow slowly into the bath. When the experiments require a long interval this procedure becomes illusive, and it is necessary to employ another mode of bath regulation.

The most simple process is to use some adjustable bath, based on the following principle: a large volume of water with a relatively small surface only takes up the surrounding temperature slowly, and much more slowly as its temperature approaches that of its environment. The adjustable bath (Fig. 80) consists:

(1) Of an iron pot, enamelled inside and out, provided with a felt jacket. This

pot is furnished with an upper outlet formed by a neck, to which is attached a rubber tube closed by a clip.

(2) Of a metallic supply apparatus which always remains in the pot. This apparatus comprises a dismountable vertical tube into whose orifice a funnel is introduced, and whose lower aperture is connected with a horizontal circular tube perforated by about 20 holes directed towards the interior and obliquely towards the top. The mixing of the added and contained waters is performed without agitation.

The thermometer, protected by a nickel case, is graduated into tenths and indicates from 15 to 25° C. The readings may be taken without withdrawing it from the water, the scale being placed upon a bar attached to the filter vessel carrier, which latter is furnished in its upper rotating part with apertures for receiving the half-filled vessels.

(3) Of a mirror holder, which is fixed by a screw to the edge of the pot and may receive the refractometer which rests upon the piece *L*.

The operation is commenced by immersing the refractometer into the water of the bath, the mirror being adjusted by the lever *G* until the water boundary is distinctly visible in the refractometer, an indication that the refractometer prism has taken the bath temperature. The refractometer is taken from the support and immersed in one of the filter vessels; the illumination is regulated by means of the mirror and the readings made for each solution to be examined by successive replacement of each in turn.

Each solution thus remains about a quarter of an hour in the bath before being measured, and is exactly at the bath temperature when the reading is taken.

After each reading the refractometer prism should be carefully wiped.

An alternative method. Forster isolates camphor by steam distillation after treatment with soda. The camphor so isolated is dissolved in alcohol aud taken to the polarimeter. According to Forster the amount of camphor contained in the liquid is given by the formula:

$$C = 2{\cdot}46826\,\frac{a}{l} - 0{\cdot}01747\left(\frac{a}{l}\right)^2$$

a being the deviation,
l the tube length in decimetres,
c the degree of concentration,

he gives the following values for a and c:

a	c
8·122°	5
16·574	10
25·406	15
34·551	20
53·927	34
74·588	40

ESTIMATION OF CAMPHOR SUBSTITUTES.

The estimation of substitutes is based upon the solubility of certain members in water. Camphor and its substitutes (these being extracted at the same time as camphor) are placed in hot distilled water. Camphor does not dissolve, but the majority of its substitutes are soluble, some in hot others in cold water.

It only remains to dry the camphor, and on weighing the difference in weight corresponds to the amount of the substitutes. The latter may be determined by evaporation of the water. They are separated and identified by successive crystallisations followed by melting-point determinations.

Extractions may also be made with ether and petroleum ether, which dissolve the mixture; the examination of the melting-points then indicates the presence of substitutes, but this only in a qualitative way.

Acetanilide may be recognised by hydrolysis with soda or potash giving aniline. By acidulation, followed by steam distillation, the camphor passes over. This method obviously presents great difficulties.

The operation is conducted as follows:

(1) The rasped celluloid is extracted with methyl alcohol, which dissolves the acetanilide and camphor.

(2) Alcoholic potash is added to the solution obtained above and the mixture boiled, thereby saponifying the acetanilide.

The reaction equation is:

$$C_6H_5NHCOCH_3 + KOH = CH_3COOK + C_6H_5NH_2.$$

By steam distillation camphor and aniline pass over.

Phosphoric acid is added to the solution of potassium acetate left in the round bottom flask and the contents distillated, the distillate being titrated. The amount of acetanilide is then calculated.

The liquid steam distillate, which contains aniline and camphor, is extracted with hydrochloric acid which retains the aniline. The camphor is dissolved in methyl alcohol or benzene after decantation of the hydrochloric acid, and the solution examined in the polarimeter. The percentage of camphor is then deduced from Forster's formula.

ESTIMATION OF THE NITROGEN CONTAINED IN THE CELLULOID NITROCELLULOSE.

The nitrogen of the nitrocellulose is estimated by Lunge's nitrometer as for a non-camphorated nitrocellulose, after drying the extracted camphor free powder. A small quantity of it is taken and dissolved in sulphuric acid of 60° Baumé.

In short, as we have already mentioned, the analysis of celluloid is a most difficult operation, and chemists, even specialists, are sometimes unable to guarantee the exactness of their analyses.

We quote here from Andès, a standard example of the analytical results for celluloid from divers sources.

Sample of French Celluloid.

Nitrocellulose	64·89
Camphor	32·86
Ash of the ether insoluble matters	2·25

Sample of English Celluloid.

Nitrocellulose	73·70
Camphor	22·79
Ash of the ether insoluble matters	3·51

Celluloid from a German Firm.

Nitrocellulose	100·0
Camphor	48·0
Zinc oxide	30·0
Castor oil	20·0
Alcohol	65·0
Blue ultramarine	0·10

CHAPTER XIV

MECHANICAL TESTS ON CELLULOID

Alongside the celluloid analyses giving the composition of the product, and so allowing its value to be approximately deduced, are the mechanical tests which, although not extending our knowledge in the above direction, offer, however, great interest from the standpoint of celluloid utilisation. It is as an object of manufacture that celluloid is employed, and such qualities as strength, elasticity, hardness, &c., are as important from the strictly practical point of view as its chemical composition.

For a long time metals have been valued by mechanical tests, and their chemical composition has been of less moment than their behaviour under the various physical agencies to which they are subjected—tensile forces, compression, flexure, torsion, &c.

It is natural to require the same with regard to celluloid, since this body may be subjected to analogous tests. The scent and feel appear to us insufficient for evaluating the qualities of celluloid, and analysis only gives us a relative mean value for the mechanical properties of this body. In our opinion there is need for the creation of a new technique to establish these mechanical properties from standard data, and it is necessary to subject this body, whose use is so widespread, to the experimental tests to which all similar substances are being submitted more and more.

This was our reason for asking M. Breuil, head of the Section au Conservatoire National des Arts et Métiers, to execute a certain number of experiments of such a character as to demonstrate the value of this new experimental method, and to establish in a comprehensive manner the behaviour of celluloid from the mechanical standpoint. We shall summarise here the results of these collected experiments.

The apparatus used by M. Breuil, which may be employed in all tests of this kind, is a dynamometer, whose description now follows:

DYNAMOMETER. P.-B.

This dynamometer may be used for tests of compression, tensile strength, slow or rapid flexure, and also for wearing trials, determinations of coefficients of friction, plasticity, &c.

The tests may be made at the surrounding temperature or at given higher or lower temperatures.

It consists of a solid cast-iron table p with perfectly smooth top, standing on two iron supports joined at their lower extremities by an iron cross-piece. The table carries the two essential parts of the dynamometer, viz. the apparatus for producing stresses and that for measurement.

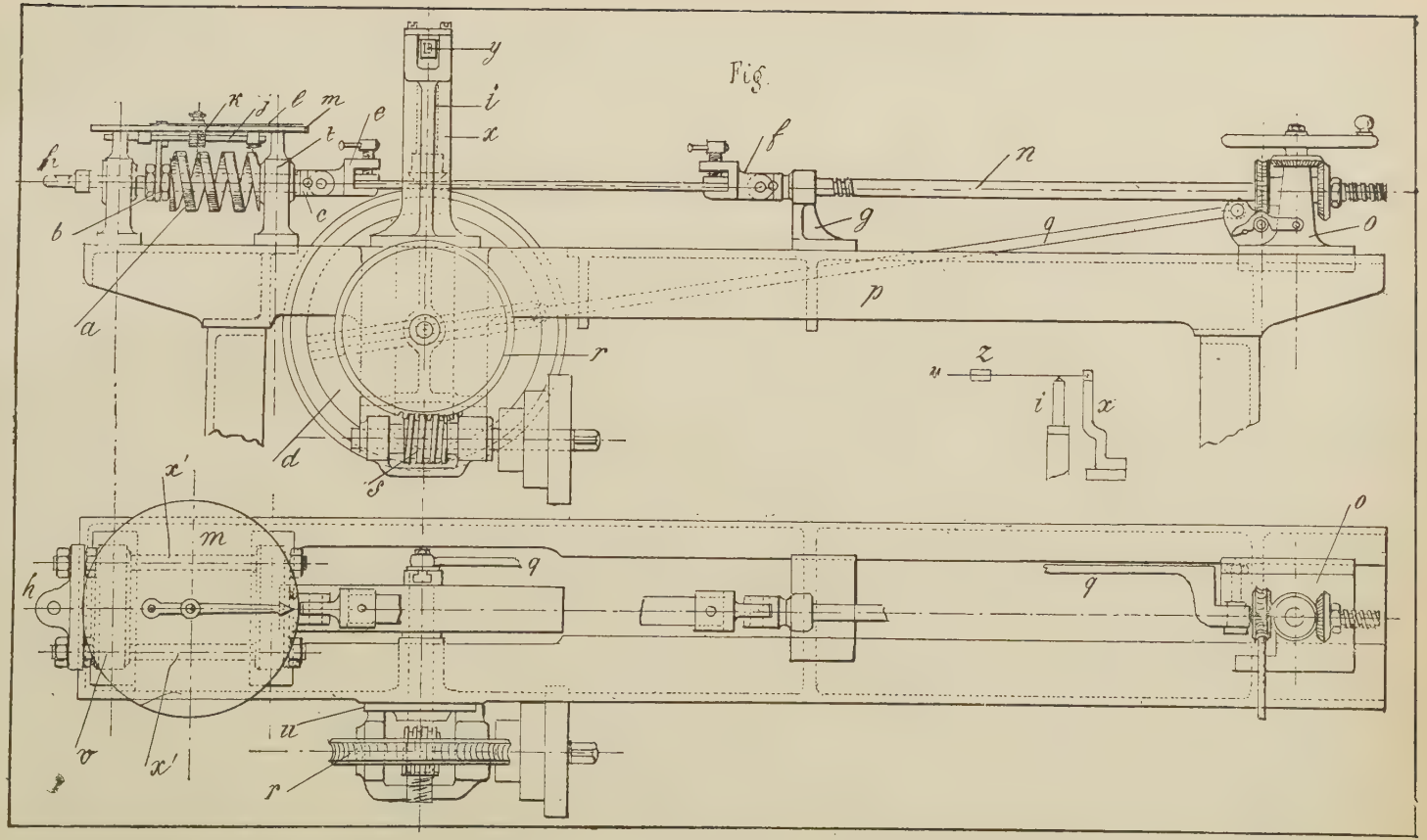


Fig. 81.

(*a*) *Apparatus for stress measurement.* The measuring apparatus consists of a special calibrated spring of tempered steel, calculated for never working with a load requiring the total power to be called forth.

This spring *a* presses against a small cross-piece *t*, being guided by a bar which lies along its axis and carries one of the jaws *e* for holding the test pieces. (Fig. 81.) Upon this rod a digit *b*, fastened by two nuts, carries a rack *j*, which in turn causes to rotate a pinion of vertical axle *k*. Upon the axle of this pinion a pointer *l* is fixed which moves in front of a graduated scale *m*.

When the piece breaks the spring is released, but the pointer *j* remains in its final position, and therefore the breaking force may always be accurately registered.

In order to be able to verify at another time the accuracy of this apparatus the spring is mounted between two small rails *x' x'* which connect the two small

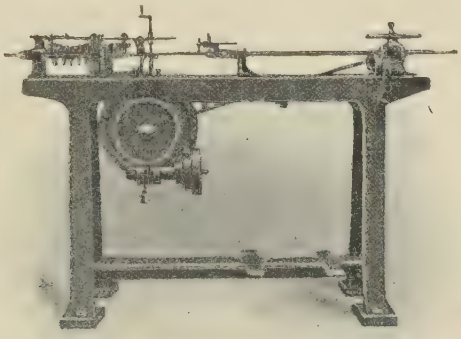


FIG. 82. Dynamometer P.-B. fitted for a Tensile Strength Test.

cross-pieces. The end cross-piece carries a screw bolt *h* and the whole of the spring and cross-pieces may be unbolted from the apparatus. By suspending the whole to the belt by a hook, and fastening known weights to the clamp *e*, the apparatus for measuring the dynamometer stresses may be checked at any time.

The spring is movable and its strength may vary in such a way as to render the sensitiveness of the apparatus equally variable. The scale carries a graduation for each spring and the pointer registers upon three graduations.

(*b*) *Apparatus for producing strains.* The piece to be tested (*e.g.* for tensile strength) is secured between the two jaws *e* and *f*, as shown in Figure 81. The latter jaw is connected to a sliding block *g* and also to a second sliding block *o* by a screw *n*. This screw may be worked at two speeds; at a high speed (for rapid work) by means of the horizontal wheel carried by the support *o*, which is driven by a turning gear, at a low speed (for developing large strains) by means of a tangent screw working the pinion situated on the forepart of the support *o*.

(*c*) *Oscillatory apparatus.* The two pieces *g* and *o* may be fixed or moved at will upon the table. Upon the lower part of *o* is attached a connecting-rod *q*,

which is worked by an eccentric wheel. If the two sliding blocks *g* and *o* be loosened and this eccentric wheel set in motion, a series of repeated tensile forces may be exerted on the test piece. The amplitude of the displacements

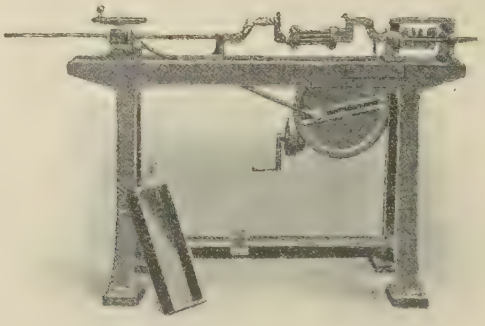


FIG. 83. Dynamometer P.-B. set up for Compression Tests.

may be varied by altering the position of the crank pin of the eccentric wheel.

The eccentric wheel is carried at the extremity of a horizontal axle upon the other end of which is keyed a pinion *r*, which works a tangent screw *s*; on the

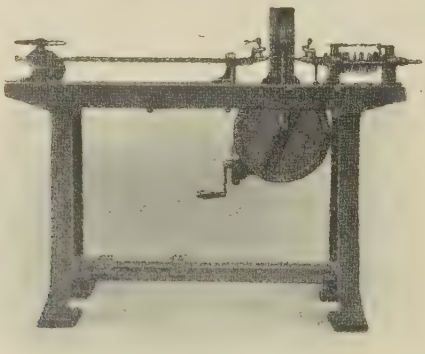


FIG. 84. Dynamometer P.-B. arranged for Flexure Tests.

axis of the latter is a small conical three-speed pulley, capable of giving variable speeds; any small motor (electrical for preference) may drive the whole by means of a small belt. The eccentric wheel may be raised or lowered vertically; the reason will be seen later.

(*d*) *Tensile trials at different temperatures.* To conduct tensile tests at the ordinary temperature, the pieces are secured between the two clamps. In the case of celluloid, the clamps are replaced by striated holders.

When the tests are to be performed at temperatures other than the sur-

rounding, the test pieces are placed in a bath which may be heated or cooled. The holders are then bent so as to pass above the bath edge.

(*e*) *Compression tests at different temperatures.* Compression tests are carried out with the dynamometer by mounting between the clamps *e* and *f* a small apparatus called "the reverser," which comprises four plates coupled two by two and arranged in such a way that when the extreme plates recede from each other the inner plates approach. The pieces for compression are placed between

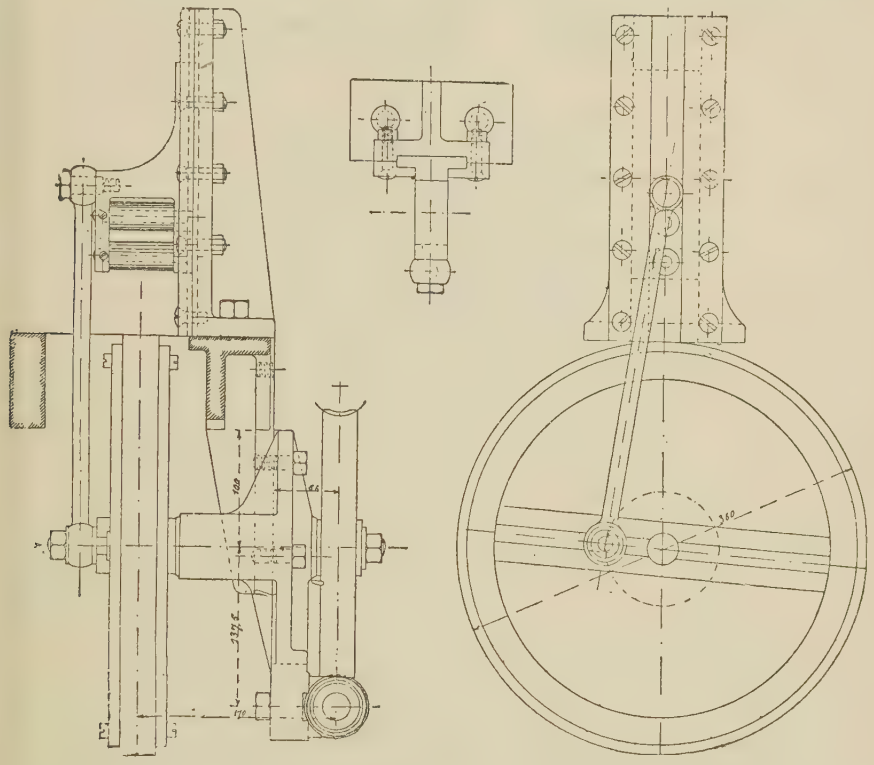


FIG. 85. Arrangement for a Wearing Test.

the two latter plates and the tests made without difficulty at convenient limit to the stresses and deformations. These tests may be made in the cold or at different temperatures in the same manner as for tensile tests.

(*f*) *Rapid flexure tests.* The strains to which certain pieces are subjected in practice are usually those of repeated rather than of slow imposition. It is therefore necessary in order to imitate practical conditions to be able to perform repeated tensile, compression, and flexure tests.

The material may be submitted to repeated flexure trials in the following way:

At first the piece is strained by means of the ordinary traction clamps *e* and *f* to a given tension.

Next, on the frame of the dynamometer is placed a small bar carrying a sliding block provided with two rollers between which the strip to be bent is passed. This sliding block is moved alternately on each side of the strip axis (or on one side only, according to desire) by means of a small connecting-rod worked by the eccentric wheel already noticed. It will clearly be seen that the

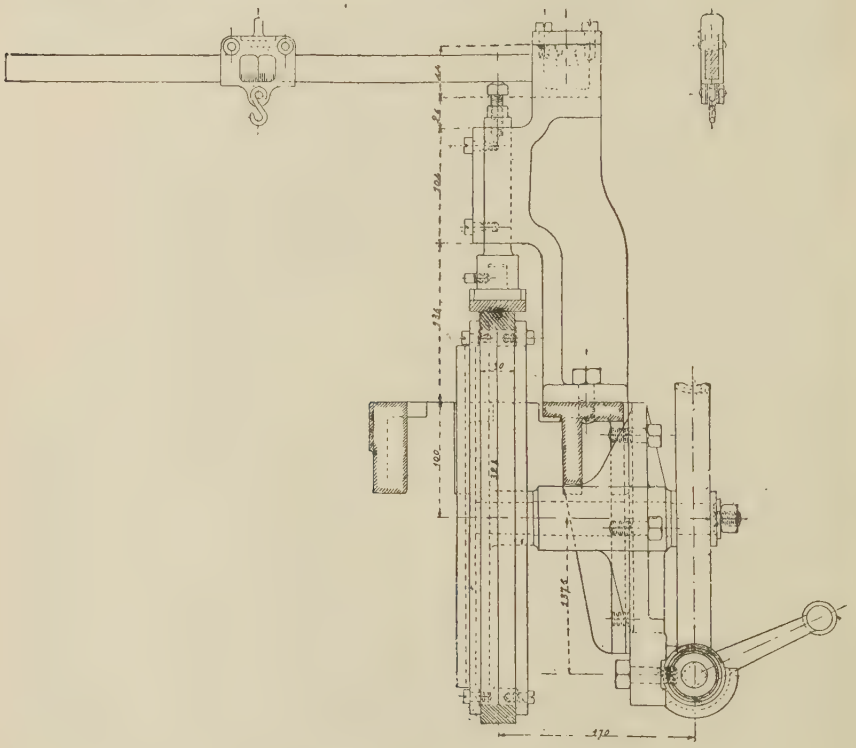


FIG. 86.

strip may be bent by known amounts, and the number of flexures endured before rupture may be noted.

The clamps or holders *e* and *f* are mounted upon horizontal axes which allow the strips to be oscillated under absolutely definite conditions.

With this arrangement may be seen the variations of strain in the strip already under tension, which correspond to a deformation. The speed and amplitude of the deformations may be caused to vary as in the tensile or flexure tests already dealt with.

(*g*) *Wearing tests and determination of the friction coefficients.* The dynamometer P.-B. allows the wearing or the coefficient of friction to be determined.

The following is the procedure for this determination:

A small stand is placed on the dynamometer table carrying a graduated

lever of the first water, upon which is placed a slide to which a known weight may be suspended. (Figs. 85 and 86.) This lever rests upon a vertical bar guided exactly through the stand and at its lower end carrying a bead which just presses upon the piece to be rubbed.

The celluloid strip to be tested is adhered to a flexible fabric which is fastened between the clamps *e* and *f*, and stretched by a convenient tension while the bead is pressed upon it.

The rim of the eccentric wheel is also furnished with a removable friction cover, and contact is established between the under surface of the test strip

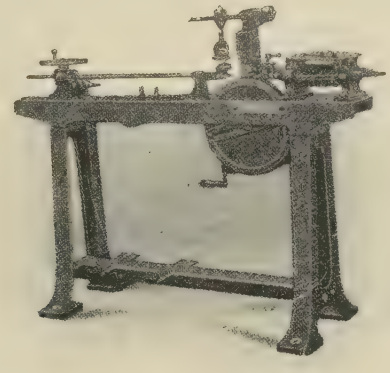


Fig. 87. Dynamometer P.-B. set up for Wearing Tests.

and the friction cover. The mechanical operations are readily comprehended; the eccentric wheel wears away the sample under conditions of speed and friction surface which may be varied at will.

The lever applying the bead indicates the pressure under which the wearing is carried out; this pressure is evidently a very influential factor in the wearing process and the latter is qualified by the loss in weight of the tested material being a function of the number of revolutions of the wheel.

The coefficient of friction of the tested material is easy to determine.

In reality, under the action of the friction-cover the strip tends to pull at the spring of the dynamometer, exerting a supplementary tension upon this measuring spring. This supplementary tension divided by the weight which presses upon the strip gives the coefficient of friction between the strip and the rim of the wheel. The removable rim may be replaced at will.

(*h*) *Boring tests.* It is easy to comprehend that a strip strained as for wearing may be perforated or cut without difficulty, if we fix at the end of the pressure-bar a needle, a sharp pointed instrument, or a knife; on the one hand this kind of experiment may be performed on a strip strained under known conditions and with an exact measure of the boring pressure, and on the other hand the perforation or cutting may be made on the free and

unstrained strip or upon the strip pressed upon the eccentric wheel. Thus many cases occurring in practice may be imitated.

This apparatus permits of obtaining exact results from the experiments executed. We may indeed plot curves for the tensile and slow compression tests, thanks to a recorder mounted upon the table of the apparatus.

This recorder consists of a drum which may turn as a function of the deformation of the tested pieces owing to a fibre which follows the exact deformation of two points on these pieces.

A special clamping arrangement is provided for this purpose.

The fibre, extended between the marked points of the two jaws which follow the extension of the strip between two marks, passes over the small support placed perpendicular to the drum and thence works the latter. The pencil carrier is moved by an arm guided by the clamp or holder attached to the measuring spring, and registers the compressions of this spring according to the movements of the drum. The diagram is thus traced automatically.

MECHANICAL TESTS ON CELLULOID BY MEANS OF THE DYNAMOMETER P.-B.

The following tests made with the dynamometer just described are of a general character, destined to inform us as to the behaviour of celluloid under tensile and compression forces.

They have no claim other than that of showing all the interest there should be in making mechanical tests on this substance. It is very desirable that these experiments should be continued and completed for every particular case which may arise in practice.

The tests have been performed on a certain number of celluloid specimens of various qualities; the majority were sheets from which strips have been taken, about 20 millimetres in width, for the tensile experiments. Let us say at once that these strips cannot be secured by corrugated clamps, which, though excellent for fibres and flexible bodies, crack the celluloid strips whose suppleness is much less and render all exact tests illusory.

For these trials jaws having striated wedges are used, such as are employed for testing hard bodies.

Compression trials are also made upon small cylinders 10 millimetres in diameter and 15 millimetres high, by means of a special apparatus which fits without difficulty to the jaws of the dynamometer.

In the tensile tests the breaking strains and elongations are measured. The curves traced with the dynamometer connecting the strains with the elongations have the form shown in Fig. 88; they are very similar to those obtained by stretching certain fairly hard tempered and annealed steels.

They may be interpreted as follows:

Celluloid rapidly attains the maximum strain it may support, and that without much deformation, although it is deformed throughout its length; it

is also deformed in a local manner—it sets (*il strictionne*), in the language of metallic technology—and the total load then decreases up to the breaking-point.

That part of the curve lying between the origin and the point *A*, appears a straight line to us; but other experiments than those mentioned are necessary in order to be certain on this point.

If the curve is a straight line it signifies that the elongations of celluloid are proportional to the forces producing them.

There would thus be an identical law to that for metals known as "Hooke's law." The strain corresponding to this point *A* would be known as the elastic

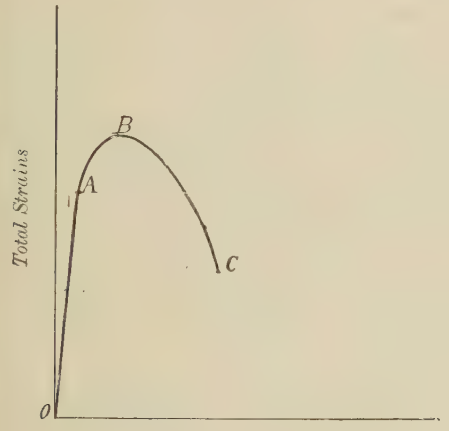


Fig. 88.

Fig. 89.

limit of the material, *i.e.* the strain after which the material ceases to recover itself completely when the strain is removed; this is a convention but it is of importance. It is in reality difficult to measure the exact breaking stress corresponding to the point *C*, and that is the reason for taking the stress corresponding to *B* as standardising the material. These, therefore, are the tensions indicated in a later Table.

Always in analogy with the experimental convention for metals, these tensions are referred to the initial cross-section of the strip tested, in order to define the unit tensile strengths of the celluloids considered. It is necessary to point out that certain celluloids break at the point *B*, *i.e.* without local setting.

In order to measure the elongation of the latter, some marks at distances of 10 millimetres are traced on the strips before the test, and the space after fracture is measured by bringing the strip fragments together; on account of the short length of the latter, the extension of 20 millimetres or two divisions is considered sufficient. The results are collected in a later Table.

Finally, the ratio of the reduction of the fracture section to the initial section of the strip is an important coefficient to determine as in the case of metals; this is given in the Table.

From the standpoint of the compression tests, they have been worked as follows; small cylinders have merely been placed between the compression plates and pressure exercised on them until the specimens have fractured. The tests in this field have not been numerous. It will suffice to point out to-day the important verifications which have been able to be carried out by tracing the dynamometer compression diagram.

This diagram has the form shown in Fig. 89; it has a rectilinear portion whose interpretation is the same as that of the traction diagram.

The strain corresponding to the point A defines the elastic limit of the cylinder tested. At this point A we have an abrupt deviation of the curve corresponding to a level track or even to a lowering, then the curve rapidly rises as far as the point B, which corresponds to the fracture of the cylinder. The latter is generally instantaneous. It is after the strain corresponding to A that the cylinder undergoes sudden alteration; with good reason, therefore, we may take this strain as the apparent elastic limit. After this we find the cylinder assuming the form of a tun and becoming ever more flat up to the breaking-point.

An agate celluloid has given as the unit elastic strain 2·4 kil. per millimetre and as the breaking force 5·45 kil.

A white celluloid has given 2·8 kil. and 10·1 kil.

A light celluloid has afforded 2·7 kil. and 12·8 kil.

The forms of the curves in each case are similar to the curve previously drawn; this type of curve is therefore a good representation of the properties of celluloid under compression.

Finally, the following are the results of the tensile tests for the celluloids studied. The compositions of the latter are given after the Table.

It follows from the tests recorded in the Table that the various celluloids may be distinguished from each other. Their resistance to fracture is seen to vary from the simple to the complex, according to their greater or less content of cellulose pulp. Since the resistances vary directly as this content, it follows that the traction test is a means of estimating the cellulose in a celluloid.

On the other hand, the elongation and setting do not appear to be a distinct function of the pulp content; a whole series of fresh observations must be undertaken for clearing up this relationship.

The problem moreover has only been scantily dealt with in what precedes; it remains to investigate the influence of all the factors which may affect the mechanical properties of celluloid, *e.g.* the geometrical forms of the samples tested, the rapidity of the trial, the temperature which plays a large part in the behaviour of celluloid, &c.

TESTS FOR ELASTICITY AND HARDNESS.

Among mechanical tests, the degrees of hardness and elasticity of celluloid are interesting measurements. These may be determined by means of the elasto-durometer, a small and simple apparatus occupying but a small space.

Elasticity. The principle of the elasticity measurement is as follows: A small ball of tempered steel is allowed to fall upon the specimen of material to be tested and the height to which it rebounds measured. The more elastic the material the greater the distance to which the ball rises, or the height of rebound h_r is in the neighbourhood of the distance dropped h_c. The ratio of these two distances $\frac{h_r}{h_c}$ is defined as the elasticity of the substance employed.

Hardness. For measuring hardness a steel point is used which is forced gradually into the given material; by measuring exactly its penetration in millimetres and the corresponding force, a means is at hand for estimating the hardness of the material.

Arrangement of the apparatus. The apparatus comprises a basal plate mounted upon three adjustable screws, and carrying a small column upon which a sliding block, itself carrying a special plate, may be displaced by means of a

I. *Tensile Tests on various Celluloids.*

Designation of the specimens	Transverse dimensions of the section	Section	Length from which to measure the elongation.	Rupture stress		Elongation		Striction $\frac{S-s}{S}$ [1]
				Total	Per sq. mm. of section	Total	Per cent.	
	mm.	sq. mm.	mm.	kos.	kos.	mm.	mm.	Per cent.
1	21·9×1·9	41·5	20	201	5·05	6.0	30·0	17·0
2	22·3×2·3	51·5	20	253	4·95	2·0	10·0	—
4	Diameter 7·8 mm.	47·8	20	205	4·3	0·5	2·5	—
5	22·3×2·1	47·0	20	238	5·05	0·5	2·5	6·4
8	22·0×1·9	42·0	20	228	5·4	4·0	20·0	16·0
9	15·0×0·35	5·25	35	20	3·8	0·5	2·5	6·4
10	22·1×2·1	46·5	20	200	4·3	2·0	10·0	24·0
12	22·1×0·3	6·65	20	58	8·7	2·0	10·0	20·0
13	22·5×0·2	4·5	20	37	8·25	ϵ	ϵ	—
14	23·0×1·3	30·0	20	193	6·45	2·0	10·0	—
17	22·2×1·5	33·3	20	182	5·45	4·0	20·0	21·0
19	22·4×2·2	49·0	20	205	4·18	5·0	25·0	—
20	Diameter 4·6 mm.	16·7	20	99	5·95	1·0	5·0	22·5
21	22·2×0·4	8·9	20	54	6·05	2·0	10·0	14·0
22	22·3×0·4	8·45	20	46	5·15	ϵ?	ϵ?	5·0
Amber Celluloid { Sample 1	21·0×1·3	27·3	20	118	4·32	1·0	10·0	—
Amber Celluloid { ,, 2	19·0×1·3	24·7	20	118	4·78	1·0	10·0	—
Translucent Celluloid	20·3×1·2	24·5	20	132 125	5·4 5·1	3·5	7·0	—
Another translucent Celluloid	15·0×1·0	68·5	35	23	4·6	2·0	10·0	—

[1] S = initial section; s = final minimum section.

Designation of the specimen	Dry nitrocellulose pulp	II. *Other substances*
No. 1	86 kil.	*Parts:* brown, 36 kil. ; transparent, 5 kil. *Colours:* ordinary brown, 468 cgr. ; chrysoïdine No. 2, 902 cgr. ; blue No. 1, 38 cgr. ; ponceau, 35 gr. ; compact bitumen, 90 gr. ; magnesia, 65 gr.
No. 2	86 „	*Parts:* brown, 36 kil. ; transparent, 50 kil. ; *Colours:* ordinary brown, 6·30 cgr. ; ordinary chrysoïdine, 32·20 cgr. ; blue No. 1, 1·30 cgr. ; violet, 1·70 cgr. ; bitumen, 2·36 gr. ; nacarat, 1·57 gr. ; magnesia, 2 gr.
No. 4	70 „	*Parts:* brown, 25 kil. ; transparent, 45 kil. *Colours:* ordinary brown, 100 cgr. ; chrysoïdine No. 2, 295 cgr. ; blue No. 1, 7·5 cgr. ; bitumen, 9·25 gr. ; magnesia, 36·5 gr.
No. 5	110 „	*Parts:* brown, 30 kil. ; transparent, 80 kil. *Colours:* catechu brown, 4·740 cgr. ; brown No. 1, 533 cgr. ; blue No. 1, 74 cgr. ; bitumen, 94 gr. *Transparent:* per kilog. of orange No. 1, galatte, 15 cgr.
Amber horn No. 8	86 „	Light zinc white, 120 gr. ; mixture No. 2, 11·60 gr. ; Lefranc cobalt blue, 20 gr. ; mineral white, 35 gr. ; urea, 1·300 gr.
Ivory No. 9	92 „	Light zinc oxide, 4 kil. ; mineral white, 2 kil. ; mixture No. 5, 10 gr.
Amber horn No. 10	86 „	Kaolin, 100 gr. ; light zinc oxide, 70 gr. ; mixture No. 2, 7 gr. ; Lefranc cobalt blue B, 5 gr. ; Ireland green B. Lefranc, 8 gr. ; $\frac{1}{10}$ orange No. 3, 106 cgr.
Rose No. 12	1 „	Light zinc oxide, 45·90 gr. ; mineral white, 18·480 gr. ; mixture No. 5, 0·980 gr. ; rose No. 1, 100 cgr.
Transparent No. 13	1 „	Blue No. 1 at $\frac{1}{10}$, 6 cgr. ; ultramarine, 392 gr. ; Benda, 0·140 gr. : Lefranc cobalt blue B, 0·070 gr.
„ No. 14	2·270 „	Brown, 1 kil. ; transparent, 1·270 kil. ; ordinary brown, 18 cgr. ; chrysoïdine, 33 cgr. ; violet, 0·40 cgr. ; blue No. 1 ; bitumen, 0·870 gr. ; ponceau, 0·66 gr. ; 3 grs. of magnesia are added.
Agate No. 17	—	Rods of various thicknesses : *Light:* 34 kil. of pulp, 200 cgr. orange No. 3, 20 cgr. red No. 1, 440 cgr. orange No. 2, 390 gr. urea. *White :* 8 kil. pulp, 1700 gr. light zinc oxide, 0·90 gr. ultramarine. *Horn :* 30 kil. pulp, 55 gr. light zinc oxide ; 4 gr. Naples yellow Lefranc, 1·60 gr. cadmium yellow No. 2 Lefranc ; 0·95 gr. compact bitumen dissolved in toluene.
Pearl No. 19	—	*Green part :* 40 kil. pulp, 44 cgr. of yellow No. 1 at $\frac{1}{10}$, 50 cgr. of blue No. 1 at $\frac{1}{10}$, 5 cgr. of green No. 2. *Rose part :* 50 kil. pulp, 72 cgr. of methyleosine V ; 6 cgr. of rose No. 3 at $\frac{1}{10}$; 280 cgr. of red No. 2 at $\frac{1}{10}$.
Cloudy amber No. 20	—	*Transparent yellow:* 60 kil. pulp, 870 cgr. of yellow No. 4. *Opaque yellow :* 330 gr. of light zinc oxide, 180 cgr. of yellow No. 1.
Ivory No. 21	—	Per kil. of pulp : 60 gr. light zinc oxide, 0·125 gr. of spooner No. 5 Lefranc, 0·035 gr. of spooner No. 4 Lefrance, 0·09 gr. of mixture No. 5.
Red and white marble No. 22	—	*Red:* Pulp, 35 kil., 1500 gr. of zinc oxide, 610 gr. mineral white, 180 gr. nacarat, 265 gr. cyanoseïne (in powder), 140 gr. of rose P (in powder), 1800 gr. of Adrianople red. *White:* Pulp, 15 kil. : 1500 gr. zinc oxide, 280 gr. mineral white, 1·5 gr. of mixture No. 5.

powerful screw. This plate is pierced by a threaded hole into which may be screwed at desire either the arrangement for the elasticity experiment or that for measuring hardness.

When an elasticity determination is required, a tube of transparent celluloid or glass is screwed into the threaded aperture, carrying a graduation and furnished at its upper end with a photographic iris. This iris may be opened at all diameters from 3 to 15 millimetres. The perpendicularity of the tube is regulated by the three adjustable screws and a spirit level placed on the tube carrying plate. Between this plate and the basal plate the specimen for impact is secured. The basal plate carries a platform mounted upon a spherical joint. A ball is placed on the iris and allowed to fall by carefully opening the iris. The fall is thus perfectly vertical.

The height to which the lower part of the ball rebounds is read. This reading is the only measurement to make. The trial may be repeated by removing the ball through one of the two small apertures provided laterally in the plate carrying the tube. A small groove in the base permits of receiving the ball if necessary.

Figure 90 represents the apparatus arranged for a hardness test with a specimen secured between its plates. The thickness of the test samples may reach 50 millimetres.

The apparatus has the advantage of only allowing the ball to fall on thoroughly tight specimens incapable of being displaced during the impact; displacement would completely vitiate the measurement.

The apparatus is both very accurate and uniform, *i.e.* for the same material and the same distance fallen through, the rebound is always the same.

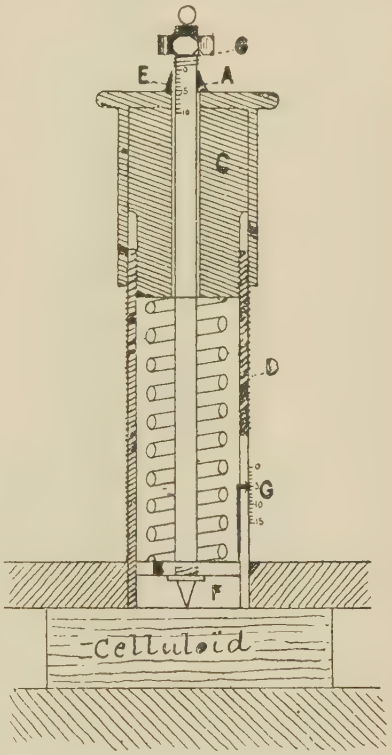


FIG. 90. Elasto-durometer P.B.

The arrangement for measuring hardness is no more complicated. It comprises a brass tube *D* which is screwed into the upper plate in place of the preceding celluloid tube. A metallic spiral spring is contained in this tube, which presses at one end upon the base *B* by a rod *A*, and at the other upon a piece *C* screwed upon the tube *D*. The rod *A* is graduated towards the upper part and serves to measure the amount by which the piece *C* is displaced relative to the tube *D* when the two pieces are screwed one upon the other; in this way we

evidently measure the amount by which the spring descends; therefore, if the spring has been calibrated, the force exerted is known.

The base B of the rod A carries a point F which, under the action of the spring pressure, penetrates into the material whose hardness we wish to determine; since this end is provided with a vernier facing a scale traced on the tube D, which is displaced proportionally to the penetrations of the point F

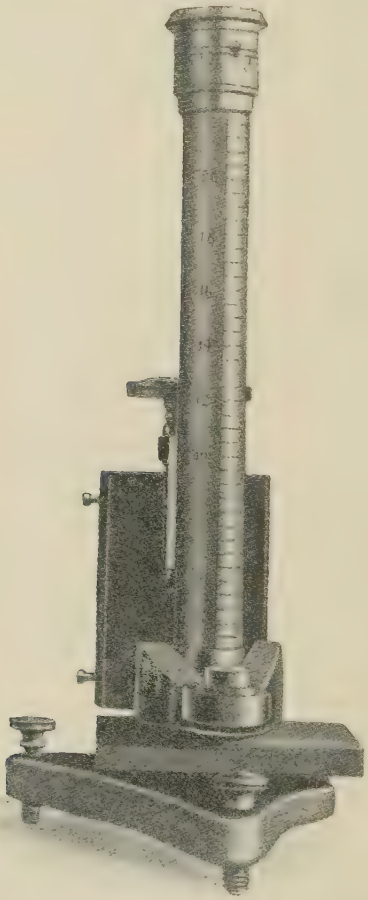


FIG. 91. Elasto-durometer P.B. arranged for Elasticity Determinations.

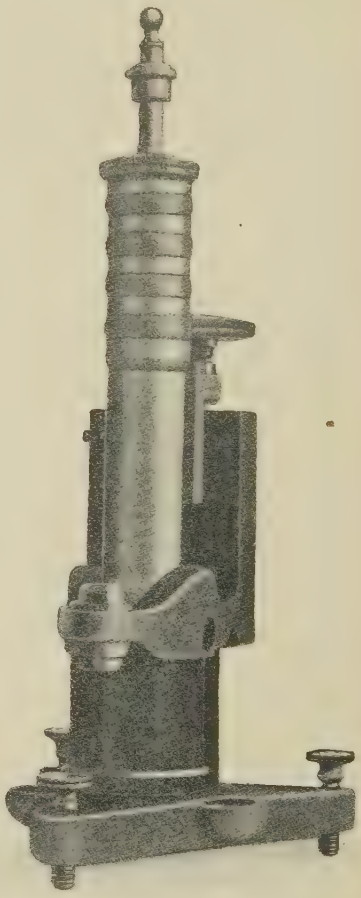


FIG. 92. Elasto-durometer P.B. arranged for Hardness Tests.

in the body, the latter are known in tenths of a millimetre during the whole course of an experiment. The two characteristics of the test are, therefore, the pressures and the amount of penetration they bring about. A nut G placed at the top of the rod A, which is threaded, prevents the rod from falling when the arrangement is not set. (Fig. 90.)

The specimen for penetration is fastened between the two plates of the

apparatus, exactly as in the case of the impact experiments. To perform a test, it suffices therefore to screw the piece C upon the tube D, to read the descent in millimetres of C upon the scale of the rod A, and by reference to the calibration table of the spring to find what force corresponds to this compression of the spring. Finally, the penetration, corresponding to each force, of the point F into the material is read on the vernier scale.

For the elasticity experiments a steel ball of 5 millimetres diameter, for example, will serve, falling through a distance of 250 millimetres.

In order to evaluate conveniently the two characteristics of hardness and elasticity, we calculate, on the one hand, the ratio of the height of rebound h_r to the distance fallen through h_e by the ball, and, on the other hand, the ratio of the pressure to the maximum penetration of the point into the material.

It is well to remark that in no sense does a relationship exist between the two factors of elasticity and hardness, and therefore it is necessary to measure each separately.

This experimental method is capable of great accuracy.

CHAPTER XV

THE EFFECT OF EXTERNAL INFLUENCES ON CELLULOID. INFLAMMABILITY

GENERAL INFORMATION.

One of the great inconveniences of celluloid, and one of the causes of the disfavour with which certain articles are, with very good reason, regarded, particularly in France, is its great inflammability. As a natural consequence, due to its constitution, this inflammability constitutes a real danger to the firms which make it, the manufacturers who employ it, and the warehouses in which it is stored.

Although the dangers of a product, which as a whole is less dangerous than ethereal oils, petrol, alcohol and many others not excluded from consumption on that account, may have been exaggerated, yet it is certain that conflagrations have been frequent, and their rapidity of propagation has often rendered assistance useless.

Generally in these fires the buildings have been totally destroyed, while the rapidity of the disaster has been great.

The works at Mannheim, those of Schmulwitsch and Hafste at Czenstochau, of Schwarts at Frankfort-on-the-Main, the buildings of the firm Friester & Co. of Berlin, and recently some New York works, where nine persons were killed, have thus been successively destroyed. At Paris, in 1904, some warehouses were involved in a conflagration and their contents to a large extent ruined.

If we have exaggerated too much the dangers of celluloid, it is also necessary to add that a large number of firms have neglected taking rigorous precautions respecting a dangerous product, and in a manufacture where eminently inflammable substances are manipulated.

The causes of the fires have in many cases been difficult to determine precisely, and most varied opinions have been expressed on the subject of celluloid dangers.

Two most important facts remain nevertheless to be clearly understood: (1) that celluloid readily ignites in contact with a flame or incandescent body; (2) that the ignition is propagated very rapidly.

These two facts are incontestable. It is useful, however, for manufacturers and merchants to know under what conditions celluloid may take fire.

There remains, therefore, the questions of spontaneous inflammability and dangers of explosion.

At this point contradictions are encountered, and we cannot do better than summarise the numerous publications of M. Will, of the Central Research

Bureau at Neubabelsberg, and of MM. Thieme, Gervais, A. Voigt, K. Voigt and Bronn.

The dangers presented by celluloid, the possibility of its spontaneous ignition and explosion, are naturally the outcome of its behaviour under those external influences to which it may be subjected.

The experiments of M. Will, published in the *Zeitschrift für angewandte Chemie* (1906, p. 1377), are interesting on this subject.

These experiments have dealt with the following points:

(1) The effect of pressure, percussion and shock.
(2) The action of the electric current and spark.
(3) The influence of light.
(4) The action of heat.
(5) Inflammability.
(6) Conditions for celluloid explosions.
(7) The resistance of celluloid to heat.

The experiments were carried out in the following way:

The samples consisted of raw and manufactured celluloid, the former in commercial sheets and rods of varying thicknesses and colour, the latter in the form of combs, hair-pins, toys, &c.

On the other hand, M. Will has investigated the nitrocellulose prepared industrially for the celluloid manufacture. Finally, the author has examined the influence of manufacturing operations upon the stability of celluloid by preparing similar specimens in the laboratory under conditions imitating, as far as possible, industrial processes. For this purpose cellulose in the form of cotton was nitrated in a small nitration turbine, then washed with cold water until perfectly neutral, washed with sodium carbonate at the ordinary temperature, and finally washed anew with cold water. This nitrocellulose in the state of pulp has been rendered stable.

It is important to insist on this fact of making stable. In the trade, enough attention does not appear to have been paid to this operation whose object is to render nitrocellulose stable towards heat. M. Will states that he has examined some nitrocelluloses destined for the celluloid manufacture which have decomposed in a very short time. The use of such nitrocelluloses is not without danger, since, on rolling, should the normally accepted temperature be exceeded, decomposition may set in. Also during compression in the block press, a temperature of 100° to 105° C. may not be applied without danger upon a celluloid manufactured from an unstable nitrocellulose. Finally, in the manufacture of combs and various moulded objects, the celluloid is often treated direct with steam at five or six atmospheres, corresponding to a temperature of 150° to 160° C. Here again a celluloid prepared with an insufficiently stable nitrocellulose will decompose. M. Will has seen some objects thus decompose, swell out and afterwards suddenly ignite, while others have endured heat very well.

The manner in which celluloid behaves under external influences evidently depends very much on its composition.

The samples analysed by M. Will had the following composition:

Nitrocellulose.	*Camphor.*	*Colours and Solvents.*
73·2	23·6	3·2
71·48	27·31	1·21
73·8	24·3	1·9
71·5	27·0	1·5

THE ACTION OF EXTERNAL INFLUENCES.

The action of pressure, shock, percussion, and friction. Pressure in the cold, shock and percussion, have only a very slight effect on celluloid.

The stamp used for explosion tests has been used for these experiments and comprises a steel anvil and a steel weight controlled vertically, which falls from varying heights known for any experiment.

This stamp acts upon a celluloid plate of about 1 decigramme placed upon the anvil, which secures that the shock is transmitted to the specimen. The mass weighs 2 kilogrammes. When a substance supports the impact of such a mass falling through a distance of 2 metres, we may rest assured that it will support every shock to which it is liable to be subjected.

The experiments have shown that no celluloid specimen has been even partially decomposed, and no explosion has taken place from the violence of the impact. Celluloid is equally insensitive to friction.

It may therefore be admitted that mechanical force cannot bring about the spontaneous ignition of celluloid.

Action of the electric current and discharge. Experiments have been successfully performed by means of a Leyden jar, an influence machine, liquid resistances, &c., under varying conditions of intensity and duration. Also electric sparks of divers intensities have been passed through celluloid plates of some tenths of a millimetre thick.

The specimens have all supported these different influences without any decomposition as regards composition. There has been revealed no trace of combustion or even of superficial decomposition. It must therefore be admitted that the electric current and discharge are without action upon celluloid.

The importance of this knowledge will be evident, since the use of celluloid in electrical work has been retarded on account of its inflammability. One would imagine that the electric current or discharge would be capable of igniting celluloid, although lightning is without action on nitrocellulose.

The influence of light. These tests have been performed by submitting various coloured specimens to the influence of an arc lamp of about 250 candle power, for a month at eight hours per day, *i.e.* about 240 hours. It was necessary, however, to screen the celluloid from the action of the lamp heat

adiations in order to establish the effect of light alone. For this purpose the uminous rays traversed a water bath which retained the above radiations.

Also, specimens of varying quality have been exposed in the open air hroughout summer to the influence of sunlight.

In each case the celluloid sustained no alteration.

The action of heat. Here arises the capital question for the treatment and reservation of celluloid.

According to certain authors celluloid is very unstable towards the action bf heat even at slightly elevated temperatures. The case of combs has been quoted which have taken fire on the heads of the persons wearing them, also hat of celluloid objects which have ignited in shop windows under the action bf sunlight. In Russia, waggons loaded with postal packages have taken fire, nd these fires have been found to be due to the presence of celluloid.

To what degree is celluloid altered by heat, and at what point will it pontaneously take fire? The question is very controversial, and we shall quote arious authorities on this point.

According to M. Will celluloid prepared under good conditions is very ermanent in the two states, raw or manufactured, to the action of moderate eat such as that from a steam or hot air pipe, an electric lamp, a neighbouring re-grate, &c. In contrast, some insufficiently stable celluloids prepared from nstable nitrocelluloses are very sensitive to the action of even a moderate eat. Certain moulding operations subject raw celluloid to elevated tempera- ures, during which partial decomposition may take place giving rise to a very nstable manufactured celluloid which is very sensitive to the influence of eat.

Some experiments made in the laboratory of the Austrian Minister of Finance, and by M. Fr. Gervais for the Russian Finance Minister, have shown hat a temperature much lower than 100° C. affects celluloid and produces a partial decomposition.

M. Fr. Gervais[1] divides the action of heat into two phases, according as the emperature is lower or higher than 90° C. Up to a temperature of 65° C. a partial vaporisation of the camphor takes place, at 65° the celluloid begins to e plastic and if the action at this temperature be prolonged, the softened ragments agglutinate afresh and the celluloid loses its plasticity.

At a temperature above 90° C. there is spontaneous decomposition with volution of heat, but without explosion. Penetrating vapours are disengaged, uickly succeeded by camphor fumes, while a thermometer immersed in the mass indicates 170° to 190°, although the heating temperature is below 100°. The object is calcined. The decomposition is much more rapid as the celluloid s raised to a higher temperature.

If this temperature is at 90°, the evolution of penetrating vapours only becomes intense after 85 to 100 minutes; if it is at 100°, the evolution attains its intensity in less than 40 minutes.

[1] Fr. Gervais, *Gorney Journal*, July 1905.

The decomposition is accompanied by a disengagement of considerable heat; nevertheless this evolution does not produce spontaneous ignition of the celluloid, but is sufficient to carbonise without flame the strong packing paper enclosing the material. There is thus no ignition of the celluloid or of the paper which envelops it, though it is evident that a current of air would suffice to kindle this paper which is burning without flame.

Normanns[1] has made the same discovery. A celluloid comb was completely enclosed in a wool flock in which was plunged the bulb of a thermometer, while a second thermometer was placed at the side. The whole was put into an oven heated with the absence of sparks. At the instant when the celluloid began to combust, the temperature of the thermometer in the wool rose to 100°, while the second thermometer only registered 40°.

A temperature elevation therefore takes place, due to the concentration of heat in the wool. This experiment shows that heat is retained in the bad conducting envelope which surrounds the celluloid object to the point of its decomposition temperature.

K. Voigt remarked that this is the case of a comb placed in hair. He declared that in the absence of this heat insulating envelope, celluloid may be exposed without harm to an intense radiant heat and without rapid decomposition. He points out, however, that decomposition may take place without intense heat radiation, and in the absence of an envelope isolating the heat, as for example in rooms heated by stoves where the temperature may not exceed 40° C. and where the celluloid is placed on thin cloth or suspended by threads. In this case there is evidently no concentration of heat involved due to an isolating envelope. K. Voigt explains it by the action of an electric spark, which is contradicted by the investigations of M. Will upon discharge action previously referred to. He admits, however, not to have experimental proof of this explanation.

Celluloid specimens behave very differently towards heat tests, and there is a need for investigating the influence played by the quality of the product in its sensitiveness towards heat.

The view that celluloid instability is due to insufficient washing has been much debated. There results from the experiments of Will and K. Voigt, and from a large number of observations, that insufficient neutralisation greatly facilitates decomposition. K. Voigt opposes this view however. We shall summarise here both series of experiments.

Will employed for his heating experiments a thermostat maintained at a constant temperature by means of an automatically regulated gas burner. The annular space of the thermostat was filled with machine oil, water or glycerine, and the temperature controlled by a thermometer penetrating into the interior of the apparatus through a double-walled cover filled with oil. The celluloid specimens were placed in the interior of the apparatus upon a plate rotating at a speed of 20 to 25 revolutions per minute, so as to produce

[1] *Chemiker Zeitung*, xxix. 1905.

a rapid air circulation in the apparatus. This air escapes by an outlet which traverses the cover. A glass aperture serves for introducing the objects and observing the temperature.

The celluloid placed on the plate was heated for 75 hours at 110° C.

The loss in weight undergone by the celluloid was determined by weighing every eight hours.

The results obtained were as follows (*Zeitschrift für angewandte Chemie*, 1906):

		Duration of heating in hours							
		72	87	88	96	104	112	120	
Loss as a per-centage of the original weight	1	8·0	8·6	8·6	8·8	9·0	9·0	9·2	Group 3*a*
	2	8·0	8·6	9·0	9·2	9·4	9·48	9·8	
	3	9·6	10 0	10·2	10·4	10·8	11·0	11·2	
	4	11·0	11·6	11·8	12·0	12·4	12·6	—	
	5	14·4	14 8	15·0	15·2	15·4	15·6	16·0	
	6	11·0	11·6	12·2	13·2	14·4	15·6	16·8	Group 3*b*
	7	9·0	10·8	13·6	16·0	18·0	19·6	20·8	
	8	13·2	15·8	18·2	20·0	21·0	22·0	22·8	
	9	37·6	38·8	39·6	40·6	41·4.	42·4	43·0	Group 2
	10	43·6	44·4	44·8	45·0	45·6	46·2	46·6	

In these experiments M. Will has recognised divergences in the results which cannot be explained by a difference of chemical composition or physical structure, and which he attributes to differences in permanence towards heat of the nitrocelluloses which have served for the manufacture of the celluloid. He has classed the celluloids into three groups according to the results obtained;

(1) Celluloids which carbonise after a few minutes' heating;
(2) Celluloids which do not carbonise on heating for several days, but experience a great loss in weight;
(3) Celluloids which support prolonged heating without carbonisation or loss of weight above the usual average.

Finally, he has divided the third group into two sub-divisions. Those of the first (sub-group 3*b*) have this peculiarity, that the curve representing the progress of decomposition is of very regular form and only rises very gradually. It evidently characterises a celluloid of very good quality and stability, whose resistance to heat is great. Those of the second (sub-group 3*a*) are much less stable, and their rate of decomposition rapidly accelerates from a certain point.

These results are fairly comparable to those obtained with smokeless powder. It is necessary, however, to take into account the presence of camphor, which to a large extent renders the celluloid stable. The preceding celluloids therefore possess a fairly great permanence towards heat.

From a practical standpoint it is interesting to have established that raw celluloid in plates, sheets, rods or tubes is much more stable than celluloid manufactured in combs, hairpins, needle cases, &c. We have already remarked that this fact is due to the moulding operations which, under certain conditions, may bring about partial decomposition. Combs resist heat the least.

Certain celluloid samples decompose at the end of 3 to 7 minutes under the influence of heat, yielding a spongy residue, while others do not sustain any decomposition even after an hour's exposure. Combs have even been found whose clear parts were more stable than the dark, such articles having been manufactured with celluloids of varying origin and quality or containing celluloid waste.

M. Will, by subjecting different bodies to the influence of heat from the electric lamp, has discovered that celluloid is the only substance which undergoes this decomposition under the action of heat.

It appears that we may determine the stability of a celluloid by measuring the deflagration temperature. We shall return to this subject when dealing with the spontaneous inflammability of celluloid.

Will and A. Voigt are of opinion that the neutrality of the nitrocellulose employed has much to do with the stability of celluloid. The nitrocellulose destined for celluloid manufacture should be perfectly neutralised and washed. It then supports prolonged exposures at temperatures exceeding 70° and 80° C. and at very great pressures. It is hardly probable that nitrocellulose imperfectly neutralised and washed will support the above temperatures and pressures without undergoing modification.

K. Voigt thinks, on the contrary, that the degree of acidity of the nitrocellulose does not count in the decomposition, and especially in the spontaneous inflammability of celluloid. He has particularly investigated whether the acid remaining in the nitrocellulose accelerates its spontaneous decomposition and facilitates spontaneous ignition. These experiments were carried out to prove that the sensitiveness of celluloid of moderate quality to heat is not inferior to that of good quality, and that celluloid manufactured with badly washed nitrocellulose is hardly more unstable than that of good quality. He has discovered that mineral colours retard decomposition. A celluloid stained with mineral colours is decomposed at the end of 8 hours' heating, while a transparent celluloid is decomposed at the end of an hour.

We see that there is disagreement between the chemists on this question of the influence of nitrocellulose acidity on the facility for decomposition. Let us note, nevertheless, that all are in accord in recommending complete neutralisation of the nitrocellulose, since otherwise the celluloid would present a soiled appearance.

THE INFLAMMABILITY OF CELLULOID.

The question of the spontaneous inflammability of celluloid by decomposition, is even more controversial than the causes of its decomposition under the

influence of heat. We shall only discuss the inflammability at slightly elevated temperatures produced solely by decomposition. By measuring the deflagration temperatures, we shall show that celluloid may take fire spontaneously under certain conditions and at certain temperatures.

It is indisputable that celluloid *in contact with flame* takes fire and burns very rapidly.

Will has compared the rates of combustion of strips of identical dimensions of smokeless powder, celluloid, and paper. He has found them in the ratio of 1, 2, 10. The heat evolved by the complete combustion of celluloid in an excess of air is from 3900 to 4600 calories; it may be compared with that of lignite which is 4000 calories, and that of pine-wood which is 4500 calories. But the rate of combustion of celluloid being nearly five times greater than that of wood, the amount of heat generated in unit time is much greater. On the other hand, this rate of combustion increases very rapidly with the temperature of the medium in which this combustion takes place; the heat disengaged in unit time increases therefore very rapidly, and the same applies to the flame temperature which grows proportionally.

This temperature may be calculated from the following data (Will):

The quantity of heat evolved by combustion in the open air of 5 grammes of celluloid caused a lead wire 0·95 mm. in diameter to melt. A brass wire, 0·5 mm., was not fused.

The heat evolved by the combustion of 1·5 kil. of celluloid waste caused an iron wire of 0·27 mm. diameter to fuse, but not a platinum wire of 0·1 mm. The temperature of combustion, therefore, lies in this case between 1500° and 1700° C. The celluloid combustion only lasting a few seconds, the amount of heat evolved is very considerable.

By all that precedes, it is seen how rapid is the combustion of celluloid and with what facility celluloid continues to burn after being in contact with a flame or incandescent body. But the further question arises as to whether this substance, on account of its sensitiveness to heat influence, may spontaneously ignite.

The opinion of many chemists, based upon occurrences under many different circumstances, and also as a direct result of experiments made on the effect of heat influence on celluloid, is that the reply to the above question must be in the negative. The experiments of Gervais, Normanns, and Will have shown indeed that celluloid decomposes under the influence of heat, but, in each case, this decomposition has not given place to spontaneous ignition.

The ignition temperature of celluloid is, moreover, much higher than that of decomposition, and Gervais concludes that the spontaneous decomposition of celluloid is accompanied by a large heat evolution, without which, however, there may be spontaneous ignition.

On the other hand, experiments have been carried out in Germany and England which, from their nature, contradict the numerous cases quoted of spontaneous inflammability. For this reason the administration of the German Post Office has had the following experiments conducted: Celluloid objects

were placed on a board and subjected to a temperature sufficient to blacken the board. The celluloid objects remained intact. In England, the administration had easily inflammable materials furnished with celluloid buttons placed before a fire. The materials burnt away but the celluloid remained intact. These tests are evidently of such a nature as to reject into the domain of illusions the phenomena of truly extraordinary spontaneous combustion related by certain individuals.

In reality a misunderstanding may easily have taken place, and that most often a chance unobserved cause has brought about ignition. There is then no question of spontaneous inflammability, but of ignition caused by contact with an incandescent body.

It is essential, indeed, to recall what has been mentioned during the study of celluloid decomposition under heat influence, viz., that the heat evolved during celluloid decomposition is sufficient to carbonise paper enveloping the celluloid and that a simple air current suffices to ignite the paper, which then communicates its fire to the celluloid mass. From this we obtain an insight into the ignition phenomenon improperly called spontaneous inflammability of celluloid. Fr. Gervais concludes that the evolution of heat suffices to bring about the flameless combustion of the paper wrapper, which the most feeble air current suffices to ignite.

The above makes explicit the majority of fires which have to be deplored in works or celluloid depôts. It follows that though celluloid is not spontaneously inflammable under heat influence, yet the latter is not without danger since a celluloid decomposition is promoted. The latter, while not capable of self-ignition, may ignite the wrapper or other substances in contact with it in the presence of a very feeble air current. Now, in the majority of circumstances this air current exists, and if the objects in contact with the celluloid are heated to redness by its decomposition, a fire will inevitably result.

Thus, in reality, celluloid does not itself spontaneously ignite and does not inflame the bodies in contact with it, but practically the fact must be recognised that celluloid may carbonise these bodies, heat them to redness, and so constitute a real danger.

We shall insist on this point, because it follows from what precedes that, in spite of the non-existence of the spontaneous inflammability of celluloid, there is need for great precautions to be taken during its preservation and particularly storage, since it is then in contact with paper, boards, or string which easily burn and ignite under the influence of unavoidable air currents. From the industrial standpoint this ignition should always be feared in the constant presence of air currents.

Gervais estimates that the decomposition temperature being much lower than that of ignition, the heat liberated by the decomposition is insufficient for bringing the mass to a temperature for determining ignition.

In practice, should the celluloid continue to be subjected to an elevated temperature after its decomposition then ignition may take place.

THE IGNITION TEMPERATURE.

Gervais has established the ignition temperatures of celluloid objects to be extremely variable. The following are those of a few objects:

Oyonnax comb	425° C.
A child's ball	457°
Hairpin	440°
Cigar case	355°

In general, white celluloid imitating ivory ignites less readily than others, and gives a greater amount of ash on burning.

Will, on his side, has established the celluloid groups previously mentioned to have variable ignition temperatures. For the first two groups it lies between 120° and 150° C. and for the third between 170° and 180° C.

M. Michotte, Engineer and President du Comité technique contre l'incendie at Paris, according to his own experiments on specimens of good quality, declares that the decomposition of celluloid may be produced between 160 degrees and 170 degrees without ignition, and that the latter is only brought about when the object is heated to redness and the evolved vapours come into contact with a flame. Celluloid has been subjected to the action of a Bunsen burner, separating the specimen from the flame by a double wire gauze, without ignition being caused.

Deflagration temperature. M. Will has determined the deflagration temperatures of different celluloids, *i.e.* the temperature at which it abruptly ignites, and he recommends this determination as a means of evaluating the quality of a celluloid. This expression of quality is taken in the sense of its greater or less permanence to heat action, and its greater or less tendency to undergo a modification in composition under the influence of a transitory heating.

The experiments were conducted as follows:

Into a thick glass experimental tube, lightly stoppered, were introduced 10 centigrammes of celluloid in small fragments. The whole was heated in an oil bath previously taken to 100° C. The bath temperature was made uniform by a stirrer, and the heating made slowly and regularly, so that the temperature should rise about 5 degrees per minute up to the deflagration of the celluloid. This temperature is noted, being the deflagration point of the celluloid tested, *i.e.* the temperature at which it suddenly ignites.

The following are some results concerning celluloids tested by Will, and classified by him into the three groups previously mentioned.

Deflagration points established:

1st and 2nd groups	Raw celluloids in plates, rods, &c., 130°, 143°, 147°, 148°
	Manufactured objects, 124°, 125°, 133°, 139°, 144°, 153°.

3rd group { Raw celluloids in plates, rods, &c., 160°, 168°, 174°, 175°, 176°
Manufactured objects, 167°, 169°, 172°, 173°. 178°, 181°.

This experimental method appears from its nature to allow of evaluating the degree of stability of a celluloid; it is simple, of easy application and sufficiently accurate. M. Will considers that it might furnish useful information for determining whether a given celluloid may be preserved without danger under the conditions which obtain in practice. By developing this method and taking into account complementary experiments, the temperature at the deflagration point, which may be taken as an inferior limit for a celluloid of sufficient stability, may be established. Will opines that this limit may be fixed at 160 degrees.

These experiments would seem to be of such a character as to fix definitely the question of spontaneous inflammability, and that for a celluloid of normal composition, *i.e.* about two parts nitrocellulose to one of camphor, the temperature of spontaneous ignition may be considered at 170°, *i.e.* the same as that of its elements nitrocellulose and camphor, which spontaneously ignite at this temperature.

The preceding experiments show that this temperature of deflagration or spontaneous ignition varies, on the one hand, naturally with the composition of the celluloid and, on the other hand, with the character of the manipulations during its transformation into manufactured objects. It should be taken into account in every case, that the deflagration temperature of an object manufactured from a celluloid of known composition is often lower than that of the same celluloid when in the raw state, on account of the partial decomposition produced during the manufacturing operations.

The question of knowing to what extent the degree of washing and of neutralisation of the nitrocellulose influences the temperature of spontaneous ignition does not as yet seem to be well established.

L. Voigt declares that up to date the facts do not justify the assumption that the defective washing of nitrocellulose increases the readiness for spontaneous ignition. A. Voigt, on the contrary, states it to be indisputable that insufficient washing and neutralisation increases this readiness. Will admits, with the majority of chemists, that defective neutralisation of the nitrocellulose favours the spontaneous decomposition of celluloid, and thinks that sufficient regard for its stability is not exercised during manufacture. Since he gives lower deflagration points for the celluloids included in his first two classes, *i.* those which carbonise most easily under heat influence or the most unstable, we are justified in concluding from his researches that the point of spontaneous ignition is lowered by insufficient neutralisation.

It would be necessary before drawing any conclusions from these controversies to complete the series of preceding experiments by performing them under every possible condition.

CELLULOID EXPLOSIONS.

Explosions due to the combustion of celluloid. Celluloid is spontaneously inflammable towards 170°, but is not explosive under ordinary practical conditions.

This affirmation is based upon a large number of experiments, and also upon the authoritative opinion of Vieille and Will, as well as upon many facts of experience. In many fires large quantities of celluloid have been seen to burn without giving rise to any explosion; some years ago, for example, in the Avenue de Saint-Mandé at Paris, 10,000 kilogrammes of celluloid were burnt without exploding.

M. Vieille has determined the combustion to be slow and unexplosive, even for considerable amounts and under condensation conditions much greater than those in practice.

The rate of combustion may vary, but there is never explosion.

This rate depends on several causes. A thick sheet burns less rapidly than a thin one, a transparent celluloid burns quicker than one charged with mineral colours; American cloth, which contains up to 50 per cent. of zinc oxide, burns very slowly. Aged celluloid which has lost a portion of its camphor burns more rapidly than that recently manufactured. In every case, however, there is no explosion worth mentioning.

We will give a brief account of the experiments of Vieille and Will which will corroborate this fact.

Vieille placed in an iron case of 270 litres capacity, having the shape of a well and furnished with a single aperture of 2·1 square decimetres, some charges of celluloid waste, which reckoned per cubic metre, were 2·5 kilogrammes, 5, 10, 15, and 20 kilogrammes. (*Vieille, séance du Conseil d'hygiène publique et de salubrité de la Seine*, May 20, 1904.) These charges were spread on the case floor as a uniform bed, and ignited by means of a powder train. A sensitive diaphram permitted the pressure developed in the enclosure during combustion to be recorded upon a revolving cylinder.

In each case this pressure did not attain 5 millimetres of water, and the flame passed through the aperture without violence, reaching to a great height.

This celluloid combustion has been compared with that of celloïdal Government powder. This gives, for a small charge of 2·5 kilogrammes per cubic metre, pressures of several decimetres of water together with a violent outburst of flame. An experience of fifteen years' manufacture nevertheless affirms that these powders do not explode in the open air. The experiments of Vieille relating to celluloid are therefore conclusive.

Will's experiments have only been performed with small quantities of material, but they are nevertheless decisive.

Weights of 1·1 to 3 kilogrammes of celluloid waste were ignited upon piles of wood in the interior of a wooden chest. The ignition brought about a very

energetic combustion, but without any explosion. The same experiments have been repeated in a closed Papin's digester. The pressure of the combustion gases were sufficiently powerful to sweep away the cover, but the expansive force did not produce an explosion.

On the other hand, celluloid subjected to pressures reaching 3000 atmospheres may explode. In particular, a specimen of six grammes was confined in a bomb of 15 centimetres capacity and ignited ; sudden decomposition ensued, and the gaseous pressure rose to 2970 atmospheres. Under such conditions, the ignition was explosive. Such pressures, however, are never attained in practice, and M. Will has attempted to explode celluloid under ordinary conditions, for example, by enclosing it in stout chests of double sheet-iron, and air-tight. In no case was an explosion obtained.

We may conclude from all these experiments that celluloid is not explosive, and that only the danger of fire has to be feared. Explosions, however, have frequently occurred in fires or in works during the course of manufacture, or again in workshops making celluloid objects. These explosions are not the consequence of the combustion of celluloid itself, but through the formation of a detonating mixture made up of the decomposed constituents of celluloid and air.

Explosions due to the admixture of dust or of celluloid decomposition gases with air. Explosions may be caused in a fire, or during manufacture, or in a workshop where large quantities of celluloid dust are generated, by the ignition of a detonating mixture formed with air.

M. Will has sought to establish the conditions under which these mixtures may be formed.

The decomposition products of celluloid vary according to the conditions of decomposition. From the chemical standpoint, the greater the pressure the simpler the products.

M. Will has brought about the decomposition of celluloid in the following way (*Zeitschrift für angewandte Chemie*, 1906) :

Various celluloid specimens were introduced into a bomb in the ratio of one gramme per 15 centimetres capacity, with a charge density of 0·067. The vacuum was made in the bomb, and flame introduced by an incandescent filament. The constituents of the mixture obtained, were as follows :

Celluloid No. 2.	
Carbon dioxide	14·4 per cent.
Carbon monoxide	47·1 ,,
Methane	14·2 ,,
Hydrogen	19·8 ,,
Nitrogen	4·5 ,,

Celluloid No. 3.	
Carbon dioxide	14·0 per cent.
Carbon monoxide	46·0 ,,
Methane	17·1 ,,
Hydrogen	17·9 ,,
Nitrogen	5·0 ,,

Celluloid No. 6.

Carbon dioxide	20·9 per cent.
Carbon monoxide	41·0 „
Methane	17·6 „
Hydrogen	13·4 „
Nitrogen	7·1 „

The inflammable gases: carbon monoxide, methane, hydrogen are present in large amounts in all these mixtures.

Another experiment made under the same conditions, by promoting ignition with a wire heated to redness by an electric current, yielded the following results:

Carbon dioxide	16·8 per cent. by volume.
Carbon monoxide	45·7 „ „
Methane	19·4 „ „
Hydrogen	10·5 „ „
Nitrogen	9·6 „ „

If air be added to these mixtures they become inflammable. The mixture of 1·7 litres of air, for example, with the latter gaseous mixture exploded under the influence of the electric spark. If the proportion of air be increased, the explosive force only diminishes when 8·1 litres of air are mixed with one litre of the gaseous mixture.

If the gaseous decomposition products of celluloid be compared with alcohol, ether, petroleum ether, &c., from the explosive point of view we shall see that all these gases behave in the same way, but that the limits between which the mixtures of air and the celluloid decomposition products are explosive are much more extended than those of the vapours compared.

According to Eitner (J. Gasbel. und Wasserversorg, 1902) these limits are as follows:

Nature of the Gas.	Limits between which the mixture with air is explosive (proportion of gas in $\frac{1}{100}$).
Celluloid gases	9·0—40·0
Methane	6·2—12·7
Alcohol	4·0—13·6
Ether	2·9— 7·5
Petroleum ether	2·5— 4·8

We see that of all the products in question the celluloid gases are those which have the widest explosive limits. Carbon monoxide and hydrogen, whose limits are:

Carbon monoxide	16·6 — 74·8
Hydrogen	9·5 — 66·3

have alone more extended limits.

If instead of evacuating the bomb air be admitted, the pressure may reach 100 kilos. per square centimetre.

If it be placed under conditions of greater pressure, easily realisable in practice, by causing celluloid to burn under a glass bell jar in presence of air, the combustion products contain nitrous vapours and hydrocyanic acid, whose presence in the gases resulting from the celluloid explosion has been pointed out by Guttmann in his book, "Explosivstoffe" (1895). The nitrous vapour content is very variable according to the combustion conditions.

The following are the results by making the combustion under these conditions:

Celluloid No. 9.

Carbon dioxide	25·8 per cent.
Carbon monoxide	38·4 ,,
Methane	5·2 ,,
Hydrogen	2·3 ,,
Nitrous vapours	23·7 ,,
Nitrogen	4·6 ,,

Celluloid No. 10.

Carbon dioxide	24·8 per cent.
Carbon monoxide	37·3 ,,
Methane	? ,,
Hydrogen	? ,,
Nitrous vapours	18·8 ,,
Nitrogen	? ,,

These experimental conditions are evidently not those of fires, although we must admit that they inform us sufficiently as to the practical conditions. The states of pressure and air access are evidently very near those of the experiment, and as they are the two principal factors which influence the composition of the gaseous mixture resulting from combustion, the experiments may therefore be considered as conclusive. The amount of air admitted into the bell jar was rather greater than that in contact with celluloid in practice, while that of the bomb was certainly less.

From all these experiments it follows that though celluloid does not explode by itself when burning, yet it gives rise to gaseous products which may form a detonating mixture with air.

We have seen, moreover, that very high pressures plus heat may give rise to explosions. Under practical conditions, however, high pressures are not realised, so that explosions known as "*press accidents*" are entirely exceptional.

Finally, in the workshops employing celluloid, dust is unavoidably formed. This dust is explosive when mixed with air like gaseous combustion products.

We shall see when dealing with the comb manufacture, that dust is produced in great quantity in the grinding and shaping workshops.

Explosions of celluloid may therefore be caused in two ways:

(1) The gases evolved in the combustion of celluloid form a detonating mixture with air.

(2) Celluloid dust explodes when ignited in contact with air.

It appears that a third case may be added, viz. that of celluloid subjected to pressures greater than 3000 atmospheres, but since this fact has not been sufficiently confirmed it has little practical value.

It follows from all which precedes that if celluloid is dangerous, it is less so as a whole than alcohol, ether, benzene, &c., which are of daily consumption, and which no one thinks of eliminating from domestic use although they are a danger in other ways than celluloid.

Celluloid is, therefore, only dangerous during manufacture and subsequent manipulation, and also when stored in large quantities.

Risks during the manufacture and working up of celluloid. The manufacturing risks are of two kinds, those inherent in celluloid itself or in the nitrocellulose, and those introduced by the primary materials employed, some of which are very inflammable, such as the alcohol or ether used in certain processes.

We shall not touch upon the risks introduced by alcohol or ether, because we should then depart from the scope of this work. The reader is referred to books dealing with these substances. Moreover, the use of ether, as in Magnus' process has now been abandoned.

The greatest danger arises during the working up of nitrocellulose, which is easily inflammable.

We have seen that nitrocellulose is mixed with water during a large part of its manufacture, and in consequence does not present any danger during these phases.

The risk of conflagration commences after the complete drying of the nitrocellulose previous to grinding and steeping. The dried nitrocellulose cakes burn easily and rapidly when presented to a fire giving a long flame. They are spontaneously inflammable at 170° C. Moreover, dry nitrocellulose is very explosive.

With the idea of avoiding this danger the Cie Française du Celluloïd still employs in its works at Stains, as pointed out by M. Séguin,[1] the process of steeping, *i.e.* the mixing with camphor before completing the press drying. Camphor destroys the explosive properties of nitrocellulose, so that with this process only moist nitrocellulose is dealt with, and therefore without danger, since the mixture is rendered unexplosive by the camphor. The Stains firm even returned to its first process after having tried the one described, which is of most general use.

M. Séguin quotes the notable occurrence that during a fire which broke out at the works some years ago, the nitrocellulose chests were burnt without the pulp being consumed. It is evidently necessary, when the ordinary process is employed, to take certain precautions when storing the nitrocellulose or manipulating it up to the steeping operation. The dangers of compression in the cake drying press are not very great, since, as we have seen, 8 to 9 per cent. of water is left in the cake.

The drying chambers constitute one of the manufacturing dangers on account

[1] Note on the manufacture of celluloid by M. Séguin, Inspecteur départmental du travail at Paris (*Bulletin de l'Inspection du Travail*, Nos. 3 and 4, 1904).

of the steam pipes present. Nevertheless, after what we have noticed previously, the habitual temperatures of these drying chambers are not of a character to ignite celluloid.

The storing of the raw material and waste is equally dangerous, on account of the agglomeration of large quantities of material. The waste is more particularly dangerous because the material is in a greater state of division than in a block or sheet, and especially because it contains no trace of water and also may have lost a portion of its camphor. From the normal proportion the content may descend to 15 or 12 per cent. or even less, according to the date of manufacture. We are therefore in the presence of celluloid containing a large amount of dry nitrocellulose, and therefore very inflammable and even explosive, while possessing a quantity of camphor often too small to destroy the explosive tendency of nitrocellulose.

While on the subject of waste, there is reason to foresee risk of conflagration at the time of rolling, which process develops more heat than with the more permanent new material, since the waste is more resistant.

In a general way, we see that the danger of spontaneous ignition during the course of manufacture is only to be feared between the drying and steeping of the nitrocellulose. Also the drying of the nitrocellulose is never complete.

Apart from this case, we are in the presence of a nitrocellulose moist and non-inflammable, or of a new celluloid, undecomposed and not spontaneously inflammable, since it is never subjected to a temperature between 160° and 170°. The temperatures during rolling and drying should never exceed 78° and 52° C. respectively. Concerning the presses, their heating is insufficient to promote spontaneous ignition. As for the heat developed during the work of compression it may be easily reckoned as insufficient, since in order to redress the celluloid the plates are heated to a temperature of 90° to 105°.

Explosive dangers need not be considered. They do not even exist in the interval between the drying and steeping of nitrocellulose, since the latter is never absolutely dry.

There appears to remain nothing but heating by an electric conductor or similar body for bringing about spontaneous ignition; in a well-constructed installation the temperature should never attain 170° unless by short circuit.

The only danger to fear is, therefore, the direct ignition of new material, and in some cases the spontaneous ignition of waste. These dangers may be avoided by precautions to be indicated later. Contact with flame may be prevented with a little care. As regards the electric spark, although the experiments of Will show it to be without action upon new celluloid, it is well to take certain precautions for preventing its contact with the celluloid and especially with its dust, since the spark may be capable of giving a flame.

CHAPTER XVI

PRECAUTIONS TO BE EXERCISED IN CELLULOID WORKS

GENERAL SURVEY.

We have seen that the contact of celluloid with flame should be carefully avoided, that contact with the electric spark should be prevented, and that certain precautions must be taken against heating celluloid waste. With a good installation and strict works management all dangers may be removed. At the outset the works plant should be constructed with the view to preventting inflammability, and minimising the consequences of a conflagration, which is ever to be feared in a commercial establishment. We shall therefore consider measures of prevention and relief.

It goes without saying that in the first rank of precautionary measures are those relating to the staff. The latter should never strike matches in the works or out-buildings, while smoking must be rigorously prohibited.

The superintendence of the engines and every case of machine heating should never be relaxed. The use of any lighting apparatus or heating by open fire should be forbidden. No workman should be allowed to deposit celluloid in the neighbourhood of an electric conductor which is liable to be short-circuited, nor of a dynamo which may throw off sparks. It has been demonstrated that a very large number of fires have been caused especially by imprudence or negligence on the part of the staff. A vigorous inspection must therefore be exercised and, as a precautionary measure, the staff should be prohibited from carrying matches or cigarettes.

The construction of the works and its plant plays a large part in the risks of conflagration. We must say, to our great regret, that we have noticed preventive measures to be much neglected in many works, and that frequently their construction is defective. Combustible material also enters too much into the construction and equipment of works; the buildings are not sufficiently isolated from each other, and the lighting and heating are often dangerous. It is however, in the interest of manufacturers to remove all chances of conflagration, and to take all necessary measures for avoiding its propagation when once started, especially as the majority of works cannot be insured. Every fire therefore constitutes a loss to the enterprise. It is not to be wondered at that Assurance Companies show less hesitation if the works are constructed and equipped with the maximum of precaution. Let us add, in order to be just, that many works are exceptions to this defect.

PREVENTIVE MEASURES.

Construction and equipment of a works. All the materials for construction should be non-combustible or lined with incombustible material. The use of what is known as fireproof plaster is absolutely without value.

Iron, brick, reinforced concrete especially, and strengthened glass, are the safest materials for construction. Wood must be eliminated wherever possible. In the plant wood must be covered, where its presence cannot be avoided (and it ought to be avoided in our opinion), by a non-combustible material such as plaster, cement or fibro-cement, thus removing its surface from the action of flame.

The ignition of celluloid, which, as we have seen, is not self-igniting except under easily preventable conditions, is less to be feared in a celluloid works than that of the neighbouring workshops, which, by their combustion, may communicate fire to the mass of celluloid undergoing treatment. The danger of this mass lies especially in the rapidity with which it burns, and with which fire is propagated in consequence.

M. F. Michotte recommends for the construction :

Reinforced cement or other resisting materials such as iron and brick, the iron being built in the brick and the girders coated with cement. We incline on our part to reinforced cement, iron having the inconvenience of expanding considerably under the influence of strong heat, thereby giving rise to dangerous deformations of the structure in case of fire.

The workshops should be as much as possible detached, and separated by a passage sufficient for avoiding the propagation of fire from one building to another, since the flames emitted during the combustion of celluloid are very extended. M. Boulin, Departmental Works' Inspector at Lyon, reports that in one notable instance during a conflagration the flames, reversed by the wind, reached the roof of another shed situated 20 metres away.

Isolation has the object of avoiding the accumulation of dangerous substances in the same building, of facilitating the emptying of the building, and of avoiding the invasion of combustion gases from other workshops. M. Michotte recommends, that if one does not desire to push this isolation to excess, then to separate the sections by protected doors of wood coated with sheet iron or, better, of wood covered with fibro-cement. He gives preference to the automatic door. These doors may be opened from within outwards to facilitate removals. The outer doors should be lined on the inside, the communication doors on both sides. The windows should be of reinforced glass, and for preference automatic. On the subject of windows it is well to remark the celluloid has been seen to ignite under the influence of solar rays traversing glass. This phenomenon may be explained by the fact that in glass there exist flaws forming lenses, which have concentrated the sunlight. The celluloid at the focus of the lens thus constituted is ignited. It is advisable to cover the glass

with white paint or to affix curtains, although reinforced glass already presents a very great security in this respect.

The staircases should be of material resisting heat and flame, and shut off from the works by walls and doors to facilitate evacuation.

The lifts should be enclosed in cages of reinforced glass or of wood coated with plaster or, better, fibro-cement.

From the installation standpoint, the motors, steam or electrical engines, &c., should be placed in an isolated building, and it is an advantage for power transmission that this building should be situated as far as possible at the centre of the works. The electric motors should be protected, and it is well to employ motors fitted, as we have indicated, for hydro-extractors, so as not to emit sparks. The electrical mains should be placed in insulated tubes. Lead pipes should be prohibited.

Electric lighting is that form which presents least danger when conforming to essential limitations. Unfortunately too many installations are defective. The mains should be insulated like those for motive power, and not be under mouldings. The fuses should be protected from dust and carefully enclosed, in order that the metal when fused may not fall upon the material.

The lamps should be fixed and as far as possible placed on the ceiling.

There should be a good water-supply in each building, and the mains should permit of easy inundation at every point where a fire may break out.

As for storehouses, they should be isolated from the other buildings and constructed for preference of reinforced cement or brick and iron.

The material should be enclosed in cases of reinforced or fibro-cement, with protected doors of sheet iron or fibro-cement.

The temperature of the drying chambers should not exceed 50 to 52° C., and is with advantage regulated automatically.

M. Séguin describes the following arrangements at the Stains works: [1]

Each drying chamber is furnished with an electric thermometer placed in the heating chamber and connected to a bell and to an indicator. This thermometer is regulated so that the electric circuit may be closed and the bell rung when the temperature in the drying chamber attains 50° C. This installation is checked from time to time in order to ensure that it will act normally in case of need.

From the standpoint of separation and isolation, the division of the workshops, all of which are situated on the ground level and constructed with iron walls, is as follows:

(1) For mixing the acids and nitration.
(2) Bleaching, steeping, rolling, re-dressing.
(3) Cake presses.
(4) Block presses, cutting machines, waste sorters.
(5) Drying chambers insulated from each other.

[1] M. Séguin, *Bulletin de l'Inspection du travail*, 1904, Nos 3 and 4.

(6) Stores for the manufacture products (6, isolated from each other).

(7) Stores for the waste (4, isolated from each other).

(8) Depôts for alcohol and methylated spirits; denaturing workshop; specimen stores.

(9) Camphor recovery plant from the old waste.

(10) Furnace room.

(11) Steam engine; repairing and adjusting shops.

(12) Joiners' shop; plumbers' shop.

All these buildings are separated by yards or passages.

The 6 stores, isolated from each other and from the works, are lighted by electric lamps placed outside and giving their light to the interior by a glass pane set in the wall of the store. This arrangement presents no inconvenience; since it is useless to have a localised lighting in these stores.

The stores for waste are constructed of four separate walls, half being sunk in the ground, arched and covered with earth. The waste is only manipulated in daylight.

The roller for the waste is surmounted by a water tank whose discharge pipe can instantly flood the cylinders.

The workshops are spacious, little encumbered, and provided with doors opening from within outwards.

In all the shops where celluloid is manufactured or manipulated, the heating should be done by hot water.

N.B. Heating by open fire must be prohibited.

Older works. In works already old, analogous measures should be taken, and the works placed in a state as near as possible to the preceding.

The partitions should be rendered resistant by coating with plaster or fibro-cement, and this precaution should apply to all combustible materials. The numerous exits should be provided with protected doors opening from within outwards.

RELIEF MEASURES.

In spite of every precaution fire may break out in a works. It is, therefore, necessary to provide means for the immediate limitation and rapid extinction of the fire.

Since an enormous amount of heat is evolved by the combustion of celluloid, with the danger of explosion by contact with air of the gases generated by this combustion, it is necessary to bring about an intense cooling of the ignited mass, so that this may not continue to burn, and to avoid all excess of air, which promotes the explosion of the gas. Moist sand and water have been recommended, and they are the most effective extinguishing agents. As the problem is especially to remove the heat quickly, water is evidently, as before mentioned, the best extinguisher. The formation of water vapour, moreover, impedes air access, and prevents the formation of detonating mixtures. Grenades and chemical extinguishers are without effect.

M. Michotte classifies the relief measures into two categories:

(1) Primary aid.

(2) More effective method.

Primary aid. In each workshop, according to its size, there should be hung upon the walls two or more buckets always full of water. It would seem useless to advise that no celluloid waste be thrown into these buckets, thus constituting a danger, but the circumstance has been exposed so many times that the recommendation is not in vain. In the passage or staircase, if such exist, or, on the other hand, in the section near the entrance, a fire station should be installed, with a pipe 30 millimetres wide, sufficient for attaining the furthest point of the building. The arrangement of the pipe upon a saddle is usually defective, since the pipe gets entangled and whirls about in the air when unwound. The American arrangement is more to the purpose, in which the pipe, instead of being wound upon a saddle, is folded a certain number of times, and then on pulling unfolds in the direction of the force. The state of this pipe must be frequently inspected, since it may be cracked owing to folding. India-rubber tubes have the disadvantage of easily deteriorating, splitting, and bursting.

Chemical extinguishers only give a very insufficient jet when used, and grenades are without effect.

A good measure of precaution lies in arranging a pipe system above each machine whose operations may be a source of danger, as done at Stains for the waste-rolling machines.

More effective method. In the works yard a certain number of stations should be established according to the importance of the works. These stations should extend round the buildings, so as not to be rendered useless by the proximity of a conflagration area. At Stains [1] they are arranged at distances apart in the yard, so that there is never more than 30 metres between any two of them. They consist of water-plugs, with joints and hose pipes, connected with tanks, which are always full.

M. E. Michotte recommends these stations to be supplied with double hydrants furnished with 45 mm. or better 60 mm. pipes, always ready for use. The system of wall water plugs in boxes appears to him defective on account of the time which the setting up demands.

The extraordinary rapidity with which a celluloid conflagration is propagated should never be forgotten.

These pipes may be applied either from the town's water, or from tanks, or by the pump feeding the machinery.

According to M. Séguin both the latter methods are combined at Stains, the boiler pumps having their back-stroke connected with the main which descends to the water tanks for the plugs.

The fireman has orders, in case of alarm, to work the taps so as to add the pump pressure to that of the fire-plug main. A jet 40 metres high is thus obtained.

The pipes should be made of canvas, those of leather and india-rubber

[1] M. Séguin, *Bulletin de l'Inspection du travail*, 1901, Nos. 3 and 4.

possessing manifold disadvantages such as price, weight, displacement, and in the case of india-rubber the lack of permanence to alternations of drying and moisture. Taps on the pipes should be avoided.

Town depôts. Large celluloid stores situated very near together constitute a particular danger on account of the vicinity to dwellings.

If we take account of the fact, based upon Will's experiments, that celluloid when manufactured into articles is usually more inflammable than raw celluloid, and that on the other hand the stores almost always contain manufactured goods, the importance of the danger may be conceived. These stores need to be guaranteed against fire risks due to celluloid itself and also against external fire ; on the other hand, the neighbourhood must be guaranteed against the risk of fire propagation when produced in the store.

Should the store be isolated from dwellings, it is quite natural to provide it with preventive and also with the relief measures indicated for works.

But an isolated store is very exceptional, especially in large towns, where most often it is in an inhabited district. It is impracticable in such a case to apply to it all the precautions taken in a works.

If the store is in a covered yard, the roof for preference should be made of protected glass, which would well intercept flame.

Water should be present in plenty, and a large water-supply with a primary relief station, analogous to those in works, should be established. The chests should be protected as in the works.

When the store is inside a building, and on a floor of it, it is more difficult to guard against fire risks in its neighbourhood. The celluloid should therefore be enclosed in protected cases which would shelter it from external flames. The chest compartments should be insulated, and the amount of celluloid in each should not exceed 50 kilogrammes. Water should always be at hand. One or two buckets, always full, should be placed in the vicinity ; near the door should be a primary aid station, and in the yard of the building a double hydrant.

The storehouse lighting is made with advantage by electricity from insulated mains, and not under woodwork even if fireproof.

Fireproof plaster is also hardly more efficient than chemical extinguishers. The lamps, for preference, should be protected as in works by panes or small glass globes. The installation should be irreproachable, and the fuses perfectly insulated and enclosed.

Heating should by preference be made with hot water. No open fire should be allowed in the store, and although danger of spontaneous ignition is not to be feared, according to experiments previously mentioned, it is necessary to avoid enclosing celluloid in the neighbourhood of flues or hot pipes, as done in the past in certain Paris storehouses. The flues may indeed contain flame and thus communicate fire to the celluloid. On the other hand, stored objects are usually wrapped up, and we have seen that strong heat may carbonise the packing paper and the celluloid which is contained in it. An unavoidable draught in the building would then ignite the whole.

As a general rule, the storing of a large quantity of raw and especially of manufactured celluloid in a building should be avoided

Municipal regulations exist moreover in this regard, but unfortunately these regulations are a little complicated, and prescribed measures whose efficacy is sometimes debatable are often impracticable and expensive. We agree with M. F. Michotte that the aforesaid measures offer a security at least as real as the regulations in question, and ensure in case of accidental conflagration that propagation is impossible.

The storing of celluloid deserves very careful consideration. Contact with flame and too great heat must be avoided, air currents should be eliminated, and an installation should be to hand, which, in case of fire, promotes an immediate cooling process on the mass undergoing combustion and prevents access of air.

The first conditions are fulfilled by removing the celluloid from flues and hot pipes, the last by arranging a sufficient number of water jets and storing in air-tight cases, whereby explosions are avoided.

It is obvious that celluloid should not be stored under a staircase, which would then become a prey to the flames and thus hinder evacuation, as in a conflagration at Paris where the exits, which should have been clear, were blocked.

The protection by plaster, cement, or fibro-cement of all the combustible parts of the store, *e.g.* tables, chests, wainscotings, &c., is a prudent measure.

HYGIENIC PRECAUTIONS.

Certain operations in the manufacture and working up of celluloid give rise to the evolution of pungent vapours or to the production of dust, which may have an unfavourable influence on the organism.

Nitration in particular gives rise to a disengagement of nitrous vapours which have destructive effects on the human system, while the decomposition of celluloid evolves obnoxious fumes. M. Vieille has investigated this decomposition from the standpoint of the toxicological properties of the gases.

The decomposition of celluloid under atmospheric pressure, he says, is attended like that of every nitrated cellulose by the evolution of large volumes of carbon dioxide, nitrogen peroxide, and carbon monoxide, accompanied by hydrogen, carburetted hydrogen, and heavy fumes formed of pyrogenous camphor products. It is a kind of distillation which is propagated at a relatively low temperature. The products of decomposition ignite in the open air either spontaneously or in contact with an ignited body, giving rise to the luminous flame which is habitually observed during the burning of celluloid. If the air is deficient, however, the distillation only proceeds in the place where the celluloid is in excess, and this spot constitutes a kind of gas producer, from which escape torrents of deleterious combustible vapours, which usually burn tranquil at the orifices or, what is more serious, invade the neighbourhood and

may form detonating or toxicological mixtures on account of their large carbon monoxide content.

The products of this distillation from different celluloid specimens and gun-cotton were collected over mercury at atmospheric pressure and gave the following contents:

	1st specimen.	2nd specimen.	3rd specimen.	Gun cotton.
Carbon dioxide	9	16·5	18·5	14·8
Nitrogen peroxide	37	16·5	38	24·7
Carbon monoxide	23	16·5	14·5	41·9

M. Will has shown that when celluloid burns under a bell-jar in presence of a limited quantity of air, the products formed contain, besides the gases mentioned, nitrous vapours and hydrocyanic acid. Guttmann ("Explosivstoffe," 1895) also gives information on the hydrocyanic acid content of these gases.

Will has found quantities of this acid varying from 3·6 to 4·9 litres per kilogramme of celluloid burned. For the same celluloid specimens the amount of nitrogen peroxide has varied up to 24 per cent. In a general way the amount of hydrocyanic acid is always small in proportion to the nitrous vapours and oxide of nitrogen.

Many celluloid objects, *e.g.* combs, are varnished with acetic acid. The objects are immersed in concentrated acetic acid, then dried upon wicker frames, either in the open air or inside a building, and heated. This drying naturally promotes an intense evolution of acid vapours.

Finally, the working up of celluloid, notably by the cutting tools, gives rise to dust production, although polishing in particular is dangerous in this respect. Besides the dust produced by the friction of the polishing machine upon the material, it is necessary to take account of that retained by the polishing rollers when the latter are constituted of cloth discs, as we shall see in the production of combs. The operation known as the "discharging of the rollers" produces a dust very abundantly laden with celluloid.

These various dangers necessitate corresponding hygienic precautions.

It is obviously necessary to take hygienic precautions during nitration operations, the latter being usually enclosed during the manufacture of the nitrous products. We have seen during our nitration study that the operators are isolated as far as possible from the nitration apparatus. The use of turbines affords great security in this regard. The nitrous vapours are carried away without the operators coming into contact with them. In other processes the operator works athwart a glass case surmounted by a hood. At Stains the mixing is made by pipes and blowers, without any danger to the workmen. This process undoubtedly offers great security.

The apparatus should, in every case, be provided with energetic ventilation, which expels any fresh vapours. A small store of milk should always be to hand in case of accident. The same applies to the acetic acid fumes in the varnishing, and the indoor stove drying as practised for a short time at Oyonnax and

absolutely condemned. When time permits, the varnishing should be performed outside, and in other cases the drying should be done in special drying chambers, heated with hot water or steam and furnished with hoods and powerful ventilation.

In every workshop, moreover, ventilation is of paramount importance.

As for the prussic acid vapours and obnoxious gases resulting from combustion, it is not means of preserving but of arresting combustion which are required for isolating the fire locality, since under such conditions access of air must be avoided rather than ventilation.

In buildings where celluloid is being worked up, the workman may be sheltered from dust by carrying out the operations which generate most dust in species of glass cages, as we shall see in the comb industry. All such workshops must be ventilated.

We have not paid too much attention in this chapter to the installations for getting rid of dust by aspiration, these having received such varied application and been utilised with such success in the textile industry. The dust may be expelled either from behind, above, or below the machine and carried away by aspiration to a collector, where it is deposited, and may be recovered by allowing to settle and then removing. The removal into the celluloid workshops should be made very frequently, in order to avoid the accumulation of celluloid charged dust which would constitute a danger. The mains may be underground so as to avoid space occupation. The net price of the plant is, in our opinion, largely compensated for by the security offered to the staff, and the decrease in fouling and wearing of the machines which results from the fall of dust upon the different parts. The economy effected by this diminution merits the attention of the industry.

As regards discharging the polishing rollers, this is indispensable and should be made outside the workshop.

Such are the precautionary measures for reducing the chances of fire to a minimum, for limiting the extent of the damage caused by fire, and for ensuring security to the staff.

We have had occasion to mention briefly, but frequently, the installations at the Stains works; these indeed deserve to be cited for their good organisation and for measures of health and safety, which do credit to a management whose public spirit, moreover, we heartily appreciate.

PART II
THE APPLICATIONS OF CELLULOID

CHAPTER I
INTRODUCTION

Raw celluloid is usually delivered to manufacturing works in the form of thin sheets, thicker plates, rods or tubes.

It must then be submitted to a certain number of operations to be formed into various objects. The nature of these operations is naturally very varied, the celluloid having received a multitude of most diverse applications on account of its properties.

Celluloid is worked up either in the warm or cold, according to the character of the articles desired.

WORKING UP IN THE COLD.

This process is performed by different machines according to the nature of the operations, *e.g.* saws circular or ribbon, shears, punches, or special cutters, divers presses. The rough objects thus obtained are afterwards worked up according to models with the fret-saw, chisel, file, mandrel, &c., then cleaned upon a wheel with pumice powder mixed with grease.

All the pieces are afterwards polished.

Polishing is performed with pulverised pumice stone, or white Vienna, upon polishing plates. When using the saw care must be exercised against overheating by sprinkling the pieces slowly but continuously with water, thus avoiding a danger in the workshops where raw celluloid is being manipulated.

The latter precaution is exercised during setting or fitting, should such be carried out.

We shall describe the various working operations during the manufacture of each class of article.

Celluloid is only rarely worked up entirely in the cold; generally the fashioning requires a combination of cold and warm operations.

WORKING UP IN THE WARM.

The manipulation of celluloid with the view of obtaining certain objects necessitates bending and shaping operations, which demand a plasticity of the material impossible to obtain without raising it to a certain temperature.

Certain articles are even obtained by actual moulding, although this operation is less employed than at first sight would be supposed.

The manipulation of warm celluloid requires a very varied plant, which may be classified in three categories:

(1) *Moulds*; (2) *installations for heating*, such as heated vats and tables; (3) *various machines*, such as presses, blast machines, &c. At this point we will rapidly review the general characteristics of the plant of the first two groups. The third group we shall describe with each manufacture, since the machine designs are innumerable, according to their requirements and makers.

Moulds. The moulds destined for shaping celluloid objects consist of two parts, usually metallic, and for their manufacture cast steel (by preference, hardened steel), red copper or cast brass are used. They are opened at one end or at both, according to the shape of the object desired. Both parts are fastened together by screwing and carry necks for introducing steam.

The firm G. L. Gagnière (Appareillage électrique Grivolas) at Paris make the majority of their models of bronze. They find it advantageous to have a metal which does not rust and which becomes more and more polished with use; steel, on the other hand, rusts and does not present that perfectly polished surface, which is so important for moulding celluloid.

Joseph Mendelsohn, of Leipzig, has attempted to replace metallic moulds by those of hard wood. The latter have the natural advantage of being cheaper than those of steel or copper; they possess the great advantage of being bad heat conductors, and in consequence absorb less heat from the hot celluloid, which allows the blowing or compressing of objects without the necessity of requiring the mould to be heated. The celluloid previously heated and softened is simply placed in these moulds, and there is no fear of deteriorating the material by excessive heating or cooling. In spite of these advantages, wooden moulds have defects which hinder their general use. They may only be employed, moreover, for rough moulds, and the latter have almost been abandoned.

Moulds obtained by electrotypy are also employed on account of their easy manufacture and cheapness.

For making a mould by electrotype we proceed as follows:

A model of wax, or of any other plastic material, is made by the ordinary modelling processes, with wire and iron rod supports. The model may thus be obtained in a single piece or in two. It is next placed in an electrolytic bath of copper sulphate, where it constitutes one of the electrodes, and where it receives a coating of copper, more or less thick, according to the duration of immersion. The whole may be recoated with nickel in order that the surface may be protected and polished. If the model has been obtained as a single piece a closed mould is formed; if made in two parts, the mould will open at one side and the edges of both parts will naturally fit accurately. Closed moulds are cut into two portions by the saw.

The walls of the moulds obtained by electrolytic deposition are not very thick

and therefore not very resistant. They are consolidated by running plaster or type metal behind them.

This operation is carried out by placing the mould obtained electrolytically upon a well-dressed piece of wood, and uniformly surrounding it by strong woodwork secured to the basal piece, so as to form a box enclosing the mould whose deep part is at the bottom of the box. The side walls of the box are placed 3 or 4 centimetres from the lower edges of the mould, and also exceed it in height by 3 to 4 centimetres.

The plaster or metal is run into this box until full. A strong mould is thus obtained. The great advantage of these moulds is that their manufacture is easy and does not require a chasing operation, such as for moulds of steel or copper, in order to obtain fineness in detail. This chasing operation is very long and expensive, while the net cost of an electrolytic mould is small. This process has the additional advantage of allowing them to be made from wax models, which is not the case with steel models.

When moulds are required for using under pressure, there is need to reinforce them by a thick electrolytic nickel deposit and to replace the plaster by foundry metal.

Rud. Stübling recommends cement as an additional material suitable for manufacturing moulds. The cement is placed in an iron box and the desired shape formed, after which it is coated with a layer of soluble glass (potassium aluminium silicate) and chalk, by which the details in all their fineness may be worked up.

Magnesia cement may also be employed, this giving very hard moulds which are very durable, present a smooth polished surface with sharp edges, and render detail perfectly.

The following composition may be used:

Magnesia	20	parts
Solution of magnesium chloride at 15° B.	21	„
Pulverised amianthus (asbestos)	10	„
Iron filings, brass, &c.	10	„

Commercial magnesium chloride is obtained as crystals. To obtain the solution of 15° B. one commences by making a solution of 32° B. and then diluting.

Although these electrolytic moulds possess the great advantages of economy and ease of manufacture, their use does not appear destined to be extensive on account of the difficulty in obtaining sharp edges for detail, as is possible in the case of metallic moulds. Moreover, they only possess a relative value, since after a few moulding operations the angles become deformed and only coarse mouldings are obtained; the mould must then be replaced. Economy on this head is largely diminished.

Heated tables and slabs. Warm tables and slabs for maintaining celluloid at a temperature to admit of manipulation are formed of plates of various

dimensions, supported upon legs of either cast or wrought iron. They may be heated by gas, petrol, alcohol, steam, or hot water. In the event of petrol or alcohol heating, they carry a tank from which a transverse system of pipes emerges perforated by holes, whereby the combustible liquid burns. In the case of steam heating, the table is furnished under its lower face with a steam coil provided with two valve cocks for the entrance and exit of the steam, and connected with a steam-supply.

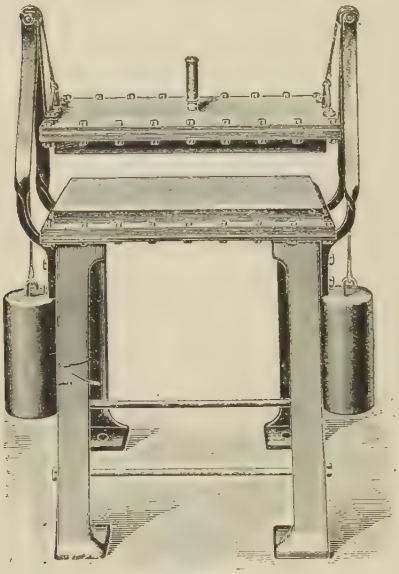


Fig. 93.

For heating with hot water, the frame of the table carries a hot water basin from which the water when cold may be withdrawn. Gas heating is much employed where steam is not ready to hand. It is, moreover, of sufficient advantage if the gas consumption is very small.

The slabs may be single or double. Double slabs allow of heating the mass upon both faces, and occasion a more uniform distribution of the heat. Their use is more particularly valuable when it is necessary to heat fairly thick celluloid plates. The distribution of heat throughout the mass is good with single plates in the case of sheets or very thin plates. In the design shown in Figure 93 the upper plate is supported by a system of two belts, two pulleys, and two equilibrium counterpoises.

Cave-Brown-Cave of London have constructed an apparatus for softening celluloid consisting of an air tight receiver containing a freely perforated bottom. Cotton, or other absorbent material, is placed upon this bottom soaked with volatile solvents and the celluloid placed therein.

Presses. A large variety of presses is required in the working up of celluloid, *e.g.* chasing presses, presses for stamping or cutting, bordering presses, presses for cutting strips, incrustation presses, &c. We shall describe the principal types during our study of the successive operations necessitated by the manufacture of the different objects.

In general, the warm manipulation of celluloid requires: (1) the softening of the material by heat or warm water; (2) working up in the press or by machine tool; (3) cooling by immersion or cold water; (4) drying; (5) cleaning; (6) polishing; (7) mounting should the object be formed of several pieces.

THE MOULDING OF CELLULOID.

The moulding proper is a process less employed for the manufacture of celluloid objects than one would believe. The reason for this is that celluloid hardens very rapidly and takes a definite shape, which it is hardly possible afterwards to change. Moulding is therefore a delicate operation, and should be carried out very rapidly. For the manufacture of many objects it has only afforded mediocre results, as, for example, in the manufacture of certain kinds of comb.

The most usual articles to be moulded are hairpins and small bars, American linen, &c.

The action of heat naturally does not suffice for bringing the material to the state of fluidity desirable for moulding, and it is necessary to have recourse to solution by one of the known celluloid solvents, with subsequent evaporation of the solvent after moulding. By using a solvent a deformation of the material is to be feared. A very consistent solution is employed, which only acts on the mass very tardily, but so continues into the heart of the mass that no deformation of the object is to be feared.

Moulding is performed by moulds and stamp screw presses or other agencies.

For small objects of low relief and not requiring compression, the moulding may be made with pincers, by simply tightening both parts of the mould held between the pincer jaws by hand pressure on the two arms.

For certain hollow objects the moulding is performed with a caoutchouc core. A caoutchouc core of the shape desired is introduced into a hollow celluloid block or tube. By heating and pressure the celluloid is moulded upon this caoutchouc core, which may afterwards be easily withdrawn. This is the method, for example, by which the handles of sticks or umbrellas imitating thorns are moulded.

Finally, mechanically extensible cores, which may be easily withdrawn, are also employed for hollow objects. The latter have the inconvenience of being a little complicated, and at present blowing methods are usually preferred.

During these later years much attention has been paid to improve the practice of moulding objects, and we shall mention some recent patented processes having for their object the removal of defects from the ordinary moulding processes.

Moulding presents particular disadvantages when the objects have thin and detached parts, such as the teeth of combs for example.

Actually the ordinary moulding process is carried out as follows: the celluloid is softened by heat, and then compressed in a mould consisting of two sections. The result is that the slender and narrow parts have to support those strains which tend to promote division and thus give rise to fissures and cracks.

On the other hand air bubbles are occluded, which also give rise to the above effects.

To avoid the first defect it has been proposed to cast the celluloid by some process, *i.e.* to remove into the thin parts some of the excess celluloid from the thicker portions. The celluloid under the influence of pressure would then fill up the cavities.

The above pressure, instead of producing disintegration effects, tends to bring about a greater cohesion of the material.

This is the process employed by the Rheinische Gummi und Celluloïd Fabrik for the moulding of combs, for example. (*See* "Moulding of Combs.")

M. Dérobert (Oyonnax) replaces this process of rigid moulds, which in certain cases necessitates the objects to be curved after moulding, by a process of the same character but in a mould affecting the definite shape of the object.

The mould is given the shape which the finished object should take, then on the side of the mould where the object has most material (the back in the case of a comb) a piece of celluloid the same length as the finished object but of less width is inserted, the whole forming a volume slightly superior to that of the object desired.

The mould is next placed under the plate of the press, which may be heated or chilled at convenience. The heating is continued the necessary time for attaining a plastic state, and then by compression the excess of material is driven into the spaces of the matrice. It should be cooled under pressure, so as to avoid any deformation of the object.

The "Bellignite" Company has adopted Lamy's process (Patent 380210), in which electrolytic moulds are recommended. According to the author a large economy in manual labour, and especially in material, is brought about by the above.

All the finish desired is given to the model, and an electrolytic cast in copper is taken. The back of a piece of tough metal is trimmed for levelling out the inequalities, and dressed so as to be placed on a steam box fixed upon the press plate and constituted so as to permit of very rapid heating and cooling. At the top of the press is fixed a smooth and perfectly plane plate, which may be lowered upon the matrice so as to close it up completely and accurately. The piece of celluloid is placed in the matrice and compressed at a known and invariable temperature, whereby all the hollows are filled without the material being able to escape.

The moulded and cooled object faithfully reproduces the model which has served as matrice, and may be softened to give desired shapes without suffering deformation.

The heating, moulding and cooling require at the most 30 seconds, and a single man may conduct two presses together. Besides the economy in manual labour which results, this process economises from 30 to 60 per cent. of material according to the objects moulded.

Electrolytic moulds do not appear to give every satisfaction for reasons previously indicated; the Bellignite Company has added to Lamy's patent by replacing the moulds with engraved moulds which allow of obtaining greater

finesse in detail. Instead of fixing the plate at the top of the press, the mould may also be directly closed by this plate. Finally a polished surface may be obtained by using a nickel coated mould or one finely polished.

By using a sectional press several moulds at a time may be worked.

The same Company has recently patented a process allowing objects to be moulded and introducing into them decorated pieces (Patent 402163). We shall discuss this patent in the chapter on "Decoration."

MM. Alombert and Bondivenne in the preceding process, utilising a smooth plate for closing the mould, found the inconvenience of the material being drawn out. To remedy this defect they recommend the following procedure (Patent 392781), which has, at the same time, the object of remedying any inconvenience due to the formation of cracks and air bubbles in the mass.

The mould being under the press and the piece of celluloid in its place, a sheet of material such as caoutchouc, &c., possessing very superior plasticity to celluloid, is applied upon the latter. During compression, this sheet touches and completely surrounds the piece of celluloid to be moulded, and prevents it being drawn out in the way produced by the smooth metallic plates. In this way between the press walls and the material there is inserted a kind of very elastic mattress and protector, which remains a fairly thick pellicle, in no wise injuring the moulding and permitting easy after-removal by mechanical means. By perforating the mould with very small holes, which allow the air to be expelled under the pressure, the formation of air bubbles is avoided.

Such are the most recent modifications carried out in the practice of moulding articles. We shall also have the opportunity of studying certain modifications relating more particularly to the moulding of combs.

Let us say at once that experience has not been able to confirm entirely the claims of the inventors. There is need, before pronouncing on the value of these recent processes, to await the verdict of practice, and it is likely that some of them will not fulfil all the promises of their inventors. The field, however, is open to research and to new processes, and these whilst practically numberless are added to almost every day.

CHAPTER II

THE MANUFACTURE OF CELLULOID COMBS

CUTTING BY MEANS OF THE SAW.

The comb manufacture is one of the most important among the applications of celluloid, since the latter has replaced to a large extent caoutchouc, horn, and tortoise-shell for this purpose.

The process of manufacture is the same in French firms as in foreign.

The principal manufacturing centre is at Oyonnax (Ain), where the majority of the inhabitants obtain their livelihood from this industry, which occupies nearly 6000 persons of both sexes.

The comb industry has existed here for more than a century, and celluloid has only been substituted for horn. The inhabitants, moreover, having been comb-workers from father to son, have acquired such great skill as to assure the success of the industry.

In France the comb is also manufactured at Etain (Meuse) (establishment of G. Petitcollin & Co.). Mannheim in Germany (Rheinische Gummi und Celluloïd Fabrik, Neckarau-Mannheim) and Aberdeen in Scotland are the principal foreign centres.

Celluloid has almost completely replaced horn and caoutchouc for the ordinary comb; on the one hand, because of its greater ease in manipulation, and on the other, because celluloid is more capable of ornamentation, in particular being stained such tints as one desires, both clear and opaque. Tortoise-shell may be imitated for cheap combs and fancy goods. Celluloid combs, in addition, may be made in every form and kind, from the simple hair-comb, pocket-comb, &c., to the fancy comb for the head-dress of ladies.

The manufacturing process is the same almost everywhere as in France, and this process differs but little in detail from that employed for the manufacture of horn combs, except that the laborious preparation of the material inherent in the use of horn, viz. cleaning, scraping, &c., disappears entirely.

The following current processes are employed in the Oyonnax district, which is the most important centre of the comb industry.

The celluloid is delivered by the manufacturers in plates of 1·30 m. by 0·60 m. and of different thicknesses and varying hues. The successive operations are as follows:

(1) Detailing; (2) tapering; (3) cutting out; (4) dressing or trimming; (5) graving; (6) pumicing; (7) curving; (8) polishing.

(1) *The detailing process.* The celluloid plate is cut into smaller sections possessing the external contours of the comb. If the comb has to be embossed,

it is cut with the saw similar to horn or wood (Fig. 94), or also placed under a screw or lever press and cut by a sharp punch as practised for leather or sheets of metal.

(2) *Tapering.* The tapering consists in thinning out the plate towards the part destined for the teeth (Fig. 94). The tapering process is performed either by a top or by means of a toothed cutter rotating at a high speed.

(3) *Cutting out.* This operation is performed at the circular saw, either by hand or by mechanical means with automatic advancement of an amount calculated according to the tooth to be formed. The small plate is secured by a

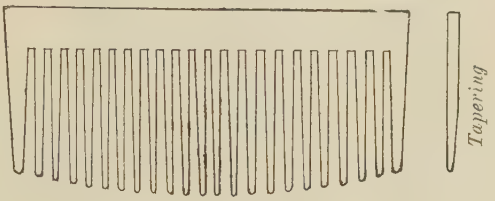


FIG. 94. Cutting out with the Saw and Tapering.

clamp, which is removed when the teeth are formed. Fig. 94 represents a comb cut out by the circular saw.

(4) *Dressing or trimming.* The teeth of the comb cut out by the circular saw have a straight rectangular section tapering towards the extremity (Fig. 95).

FIG. 95. The Filing of Teeth.

The dressing process is to round off the angles and to point the teeth, and is performed by a specialist known as "the dresser," who uses a particular kind of file known as the grêle (Fig. 96). The operator trims all round the tooth by means of a triangular file (*le carrelet*). He dresses the base between the teeth by means of a widening tool (*le revidure*), and rounds off the angles with the grêle. The outlines of the comb are shaped by a grêlot, which is a file of the same type as the grêle.

(5) *The graving or engraving process.* The corners and edges of the comb back are finished and smoothed by the engraver at a mill revolving at great speed. The engraver also ornaments the comb at the mill with borders and designs should this be necessary.

(6) *Pumicing.* This operation consists in rounding and smoothing the edges, by removing the traces left by the dressing and engraving tools.

The pumicing is made by moist pulverised pumice powder on a roller formed of cloth discs sewn to each other. This roller is mounted upon an axle, the

whole forming a kind of cloth mill about 5 to 10 cm. thick, and placed at the centre of a wooden trough containing a thick liquid made up of pulverised pumice and water. The roller turns at a speed of 800 to 900 revolutions a minute. The operator emerses the comb in the pumice mud, and holding it in

FIG. 96. The Dressing Tools.

A. File (Grêle) for large teeth. B. File (Grêle) for fine teeth.
C. Widening tool (Revidure) for trimming the interspace.
D. A dressing file (Grêlot) for shaping the comb outlines.
E. Coarse file (Carrelet) for shaping the teeth previous to using the grêle.

both hands presses it against the roller in every direction, repeating the operation several times for each face of the comb.

The roller may be replaced by a pumicing machine.

Curving. It is by this operation that combs acquire their shape.

Combs destined for the feminine head-dress receive a special curvature, which permits them to be adapted more readily to the contour of the head.

The curving process is usually undertaken by women; it demands much practice, because it is upon this operation that the particular brand of the comb depends, and every comb, even if well finished as far as this point, loses its value badly curved.

The comb is at the outset conveniently softened by heating towards 80° C., either dry or in hot water according to thickness. Usually the softening is made dry either by a gas heater or charcoal. The softened comb is then placed in a wood or metal mould, where it is kept some time by means of a small cloth strip and upon which it is allowed to cool. On cooling it should definitely retain the imparted shape. The cooling is fairly rapid, and on this account the operation does not require a large stock of moulds having the same curvative.

(8) *Polishing.* This operation is performed by a roller mounted as for pumicing, but revolving a trifle slower and made of chamois in place of cloth. Cretonne (a kind of French linen from Normandy) may also be employed. The roller is painted with a special paste whose bases are grease and tripoli.

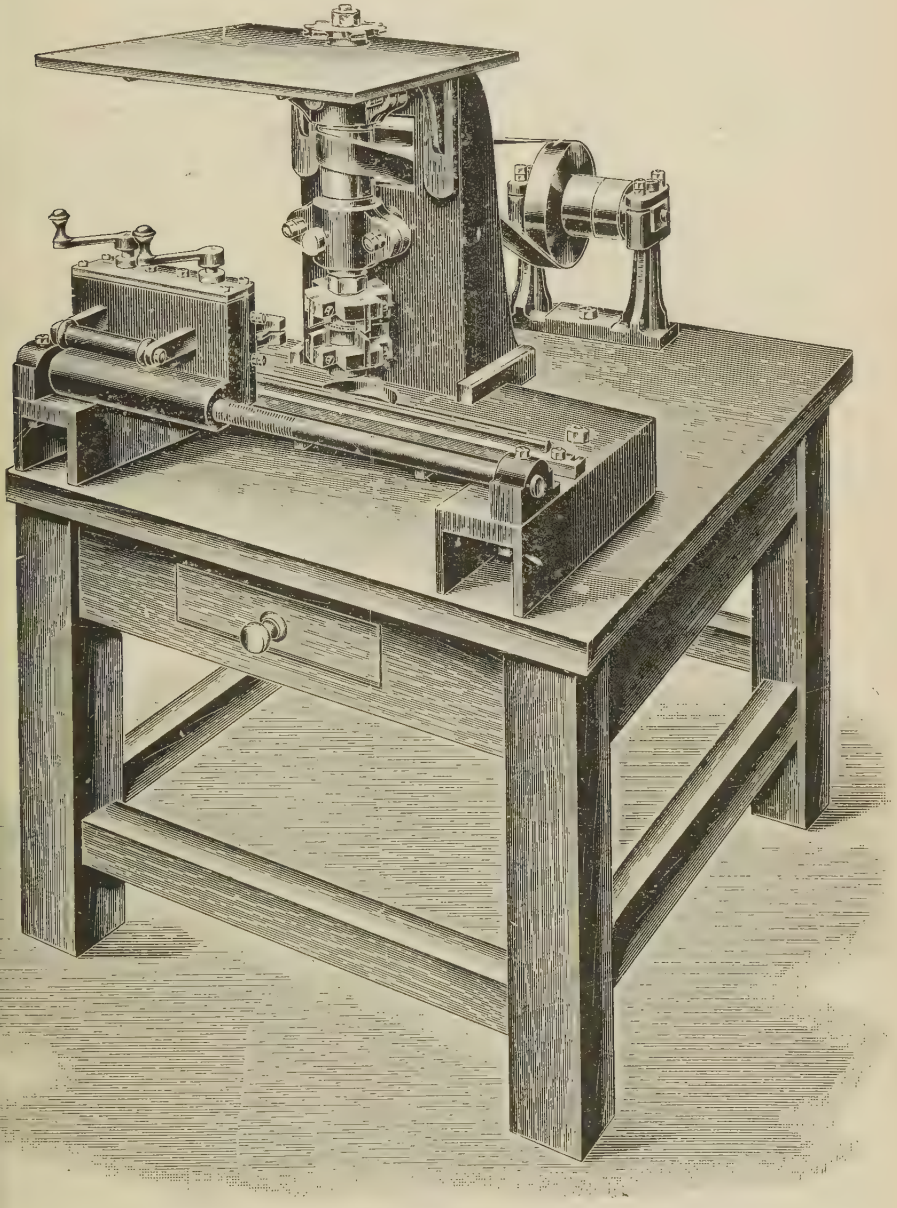


FIG. 97 The Shaping Machine.

The above manufacturing process is that employed in the majority of countries where the comb is manufactured, and is applied likewise for large hair and ornamental combs.

AUTOMATIC MACHINES.

Automatic machines will obviously afford a much greater daily production than by hand labour, especially for large hair combs which require a less variety of operations than fancy head dress combs.

The shaping or tapering of the comb may be done by machine. Figure 97 represents a machine constructed by Claussner of Nuremberg, specially

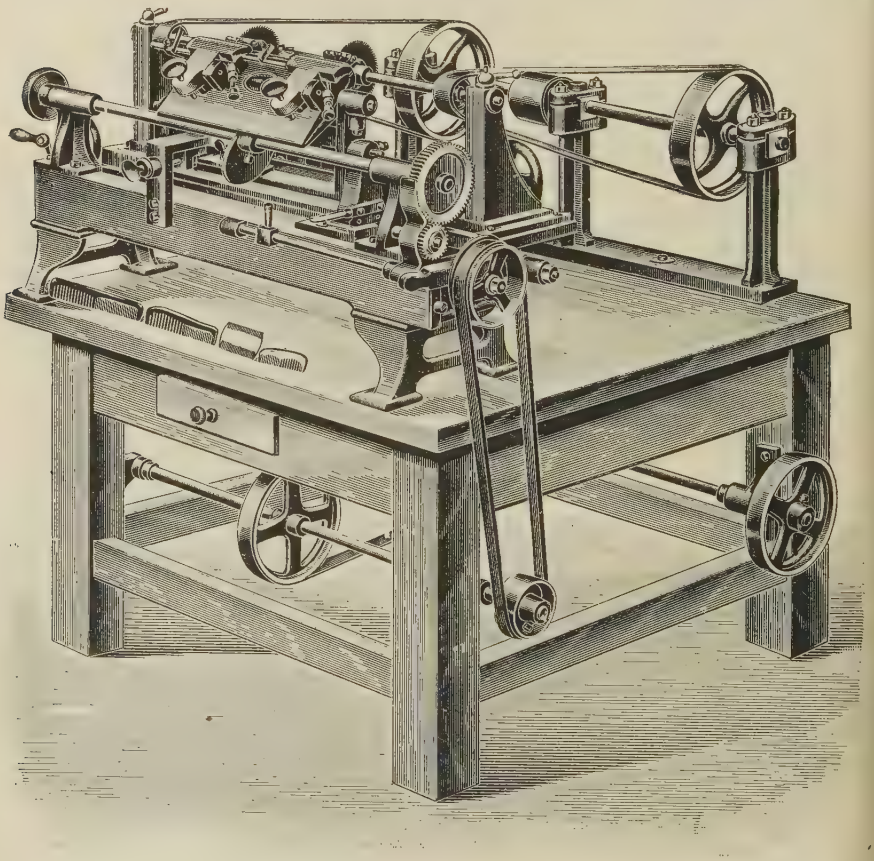


FIG. 98. Claussner Machine with Double Cutter.

adapted for this work and in particular for tapering large hair combs. It permits the comb to be thinned to about half its original thickness.

I principle it comprises a vertical shaft carrying a pulley which is belt driven, and whose base carries a cutting tool having four blades of high speed

steel. The comb is firmly held in a vice while the blades, rotating at great speed, enclose the comb at each passage. The operation is performed upon both sides of the comb while the older machines taper on one side only. There may thus be produced about 1000 pieces per day of ten hours. The requisite

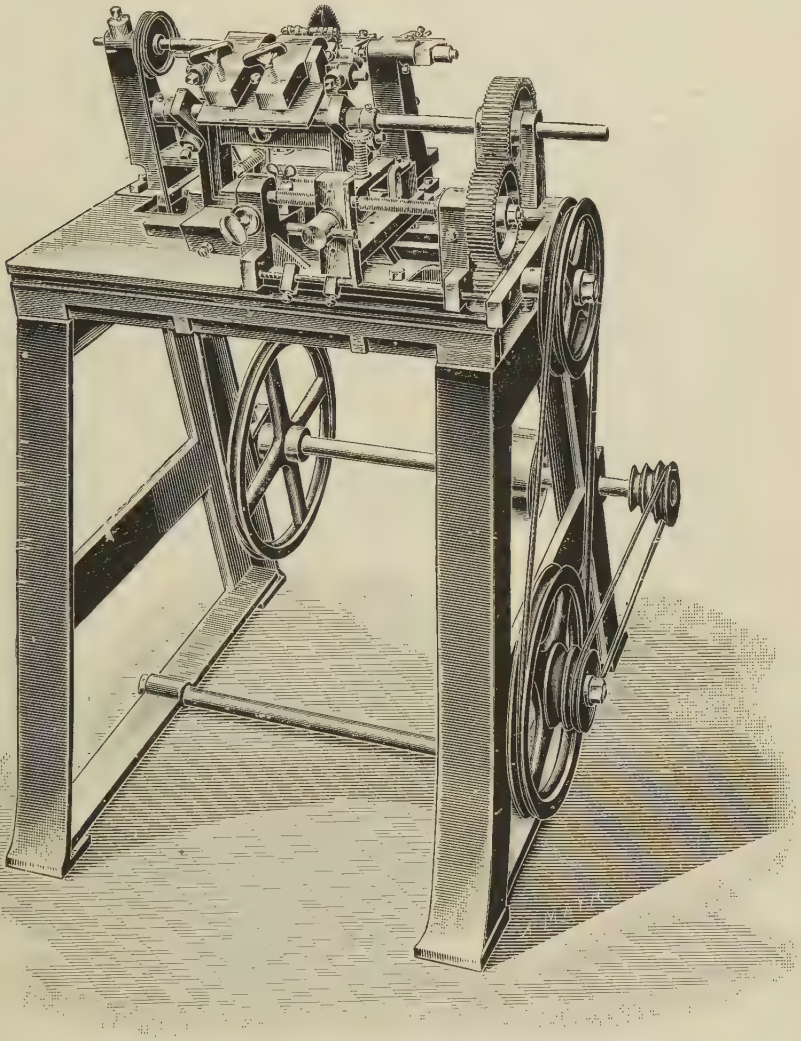


FIG. 99. Machine with Single Cutter.

power is $\frac{1}{4}$ H.P. The driving is by belt, and a youth may superintend this very simple work.

The cutting out operations are also made with automatic machines. The following machine constructed by Claussner automatically cuts out coarse and

fine teeth for every kind of comb (Fig. 98). It works with two saws which simultaneously cut out the coarse or fine teeth.

The combs are introduced from above so that the saw cuts them from below, just as in the case of non-automatic machines, and the tool follows exactly the curve of the comb by means of a gauge.

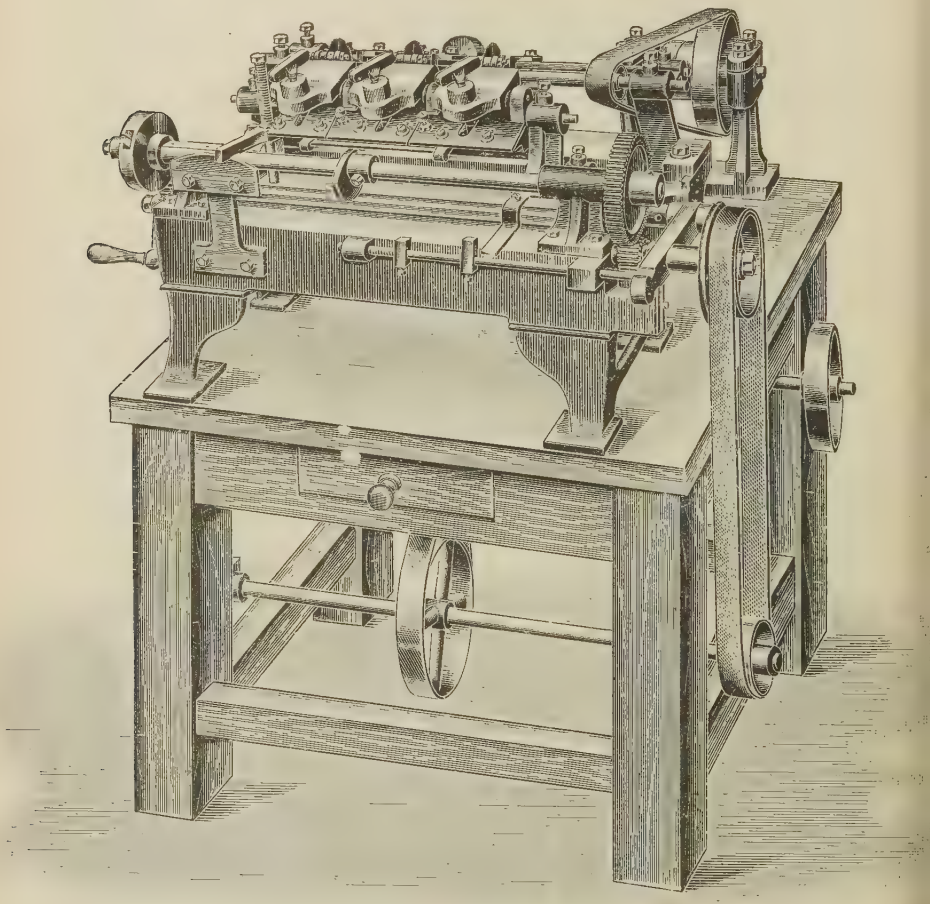


Fig. 100. Claussner's Triple Cutting Machine.

A very large production may be obtained with this machine, which varies with the nature of the combs and teeth. For large hair combs, the production for coarse teeth may reach about 1000 pieces per day of 24 hours; for fine teeth, 400 to 500 pieces. For small toothed combs there is an average of 400 pieces; for fancy head dress combs, 400 to 500, and for pocket combs, 1000 pieces.

The requisite power is $\frac{1}{4}$ H.P., and a youth or girl may conduct 4 machines simultaneously, thus effecting considerable economy in manual labour over the

older non-automatic machines. This machine is also made with a single saw, and although its capacity is halved, a single operator may superintend 8 to 10 machines at a time (Fig. 99). This machine is entirely new, its appearance dating from the summer of 1909.

The same firm also construct an automatic machine with three saws for small

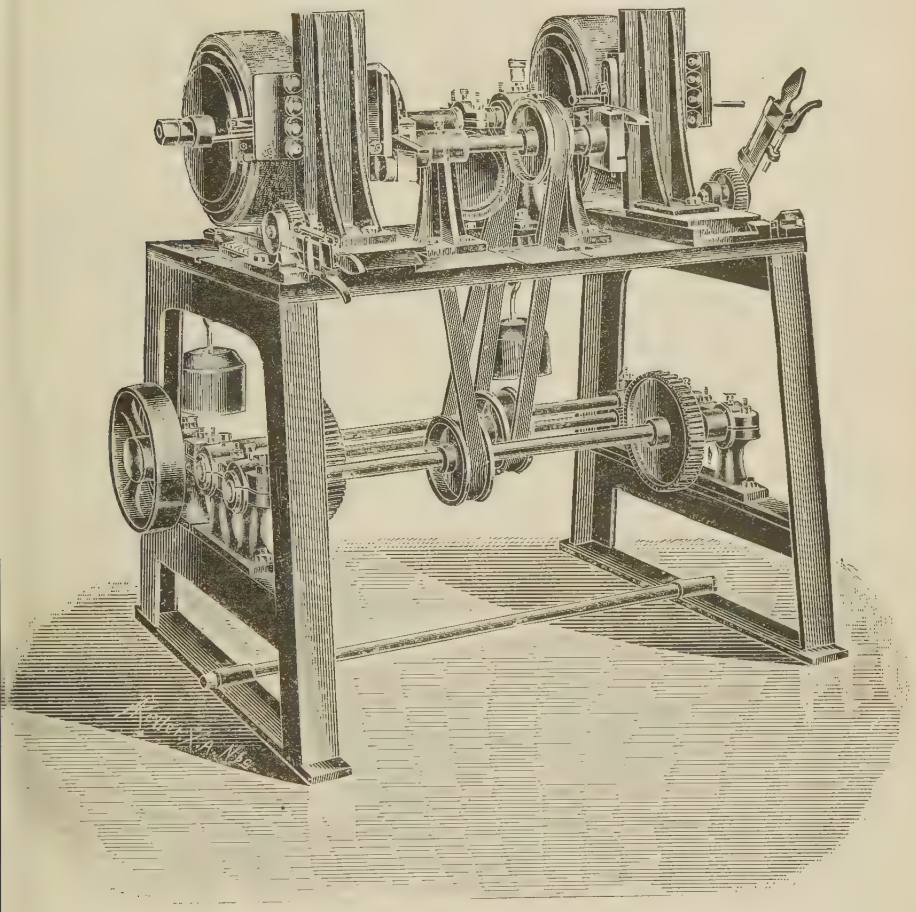


FIG. 101. Pouncing Machine.

toothed combs (Fig. 100), which may cut 12 combs at a time and produce about 1000 pieces per day in place of 400.

The mode of working is the same, but to each comb clamp 3 or 4 combs are affixed, *i.e.* 12 in all. This machine has the advantage over the roller cutters, that if one saw is defective all the 12 combs are not thrown out of action at the same time. The requisite power is $\frac{1}{4}$ H.P., and an operator may manage 6 machines at once.

In all these machines the circular saw may be replaced by any cutter whatever for the shaping operation.

Pouncing is performed automatically by presenting the combs to rollers with a special mechanism.

The apparatus constructed by Claussner (Fig. 101) is an automatic machine for pouncing. It consists of two rollers made of buff leather and two comb carriers, which have a horizontal translation motion from back to front, *i.e.* towards the rollers by means of ordinary dovetail slides.

A counterpoise adjusts and supports the comb carriers so as to bring the combs against the rollers.

The machine makes the pouncing very rapidly, and the teeth are ground at the same time.

This machine is naturally very easy to manage, and no matter whether the operator be a child or girl two machines may be worked at the same time without demanding any skill. No precautions need to be taken, and the comb cannot get loose from the comb carrier. On account of friction the machine requires a power of 1·5 to 2 H.P.

THE TWINNING OR PARTING OF COMBS.

A second process, now in vogue for some years, has for its object the avoiding of the important loss of material which results from the preceding operation.

The cutting process as carried out above not only necessitates as waste that resulting from dressing and filing, but also all the material in the interspaces between the teeth. This material cannot afterwards be recovered as waste, and utilised for inferior qualities of celluloid after being worked up again as described in the chapter on waste, or treated for extracting the camphor. The twinning process, which is by far the most important, avoids the loss occasioned in cutting out, by utilising the sawn out parts which form the comb interspaces for the teeth of another comb. This very ingenious process requires new machines known as twinning machines, and is carried out in practice as follows :

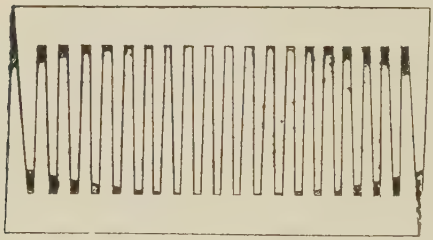


Fig. 102. Twinning or Parting.

The plate, instead of acquiring the contour of a single comb, is made into the shape diagrammatically indicated. It is next placed on the carriage of a twinning machine, being firmly secured to this at the edges. By means of a blade system, and an automatic advancement to be described later, the machine produces a continuous cutting in the plate (Fig. 102).

It only remains to separate the two combs whose teeth fit alternately, and by this means no material is lost.

Until recent years twinning machines only made teeth of square section, the plate operating in a direction perpendicular to the plate surface ; in consequence the comb had to be submitted to the delicate process of dressing.

To-day machines are used known as " Twinning Dressing Machines," which fashion conical teeth.

These machines only serve for making straight combs with teeth of uniform length. Bent combs are made by a machine called a " Bending Twinner," which makes a row of teeth plumb, the blades falling vertically, and not a row of dressed teeth. This machine tends to be replaced by others making bent

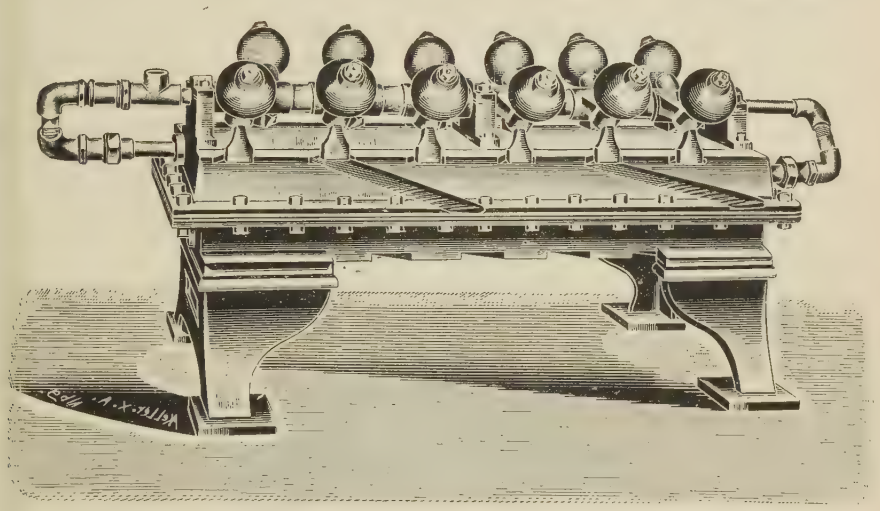


FIG. 103. Claussner's Heating Apparatus for Shaping the Extreme Teeth.

dressed combs, whose row of teeth is identical with that of the Twinning Dressing Machine, but in addition follows the bendings of the combs.

The comb obtained by twinning, is passed under a shaping machine which goes over the extremities of the teeth by means of an arched blade (Fig. 103).

The teeth untrimmed by the machine should be dressed at the mill, and this process consists in pointing and rounding off the teeth by a system of cutters. This operation has been superseded by the machine which both twins and trims.

Graving or Engraving. This operation is the same as the preceding. Since it requires a large experience on the part of the engraver, who must by his eye, unaided by any other guide except his good taste, shape the different designs upon the comb at the mill, machines have been proposed for this engraving operation. The above machines perform special work which it is impossible to do by hand.

Pouncing. This is performed as previously described. It may also be made with a pouncing machine having a buff roller (Fig. 101). This machine

replaces the older hand pouncing with advantage. The teeth are rounded off properly without fatiguing the operator, and a large output secured.

Curving. This is done by hand as described above.

Varnishing. Next follows the varnishing process or passing through an acid, which gives brightness to the combs, particularly in the parts inaccessible to the polishing roller. For this operation we utilise the property possessed by mixtures of alcohol and ether, acetene and fatty acids, and notably acetic acid, of dissolving celluloid. The combs are immersed in an acetic acid bath, from which they are almost immediately withdrawn, so as to bring about a superficial action only.

The comb may be dried on wicker work or in the open air.

This operation is performed by preference on moist or cold days in well-heated premises, so as to avoid the comb bleaching under the action of the cold, moist air.

Polishing. Finally, the polishing is done as above described. It may also be carried out at the polishing machine.

Ornamentation. Fancy articles are decorated in various ways by incrustations of metal, paste (of jewels), &c. This is the work of the mounter.

The preceding processes are applied without appreciable alteration, save naturally in curving and ornamentation, to large hair combs, which are cut out or twinned, and then finished in an identical manner to the above.

TWINNING MACHINES.

We have already seen the nature of the twinning process.

A certain number of machines have been designed for this operation, all based on the same principle, and derived more or less directly from the Lacraz patent. The chief machines are those of Bondet, Augée, Meeh, Claussner, and Convert.

The principle of these machines is as follows:

Two punches (one in some machines) are connected by rods to two cams or two eccentrics supported upon a shaft. These two punches carry at their lower extremities two removable knives or blades. These blades by the movement of the cams cut the material.

A carriage arrangement bears the celluloid plate for twinning. This carriage is moved by a rack, or by a cog-wheel and rack, which cause it to advance exactly by the thickness of a tooth after each revolution of the shaft, *i e.* after each tooth cut. The movement may be communicated by hand or by means of a screw, or, better, automatically. A lever or cam arrangement, taking its motion from the shaft, can work the carriage and cause it to advance by the amount desired. At the end of the stroke the carriage is returned by hand, or preferably by a click and ratchet wheel, which brings it back automatically. The rack should be particularly attended to and perfectly adjusted, so as to avoid cutting during the movement.

Such is the principal of twinning machines. The application varies naturally according to the makers. We give below a description of some of the machines.

MACHINES FOR TWINNING BUT NOT FOR DRESSING.

Claussner's machine. Claussner, of Nuremberg (P. Bouchhotz and Co., of Paris), make a special plant for the comb manufacture, which has been very well tested and is of very extended use.

The automatic twinning machine "Perfect" is used for cutting hair combs, dress combs, children's combs, and fancy combs (Fig. 104).

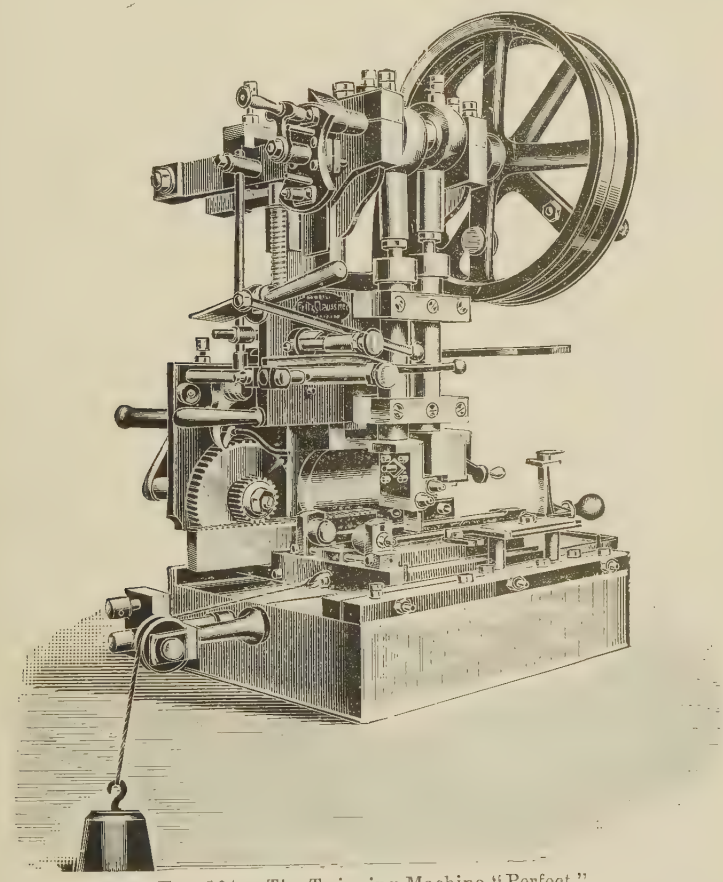


FIG. 104. The Twinning Machine "Perfect."

The machine works with a single pair of knives. Each of the knives consists of a removable blade. The punches are connected to a shaft by two cams secured at 180 degrees to each other, so that one of the knives is lowered while the other is raised. The shaft carries the pulleys, one fixed, the other free, and is driven by a belt. This shaft carries a third cam, which acts upon a rod connected

to a lever system working a ratchet. This ratchet is geared with a cog-wheel carrying on its axle a toothed pinion which works a rack. This rack drives the carriage. By this arrangement the machine may cut equally well both coarse and fine teeth without two racks having to be requisitioned. A simple hand movement suffices to make the pinion advance the desired width, and it is unnecessary to advance the carriage any further by hand or to modify the working of the eccentrics.

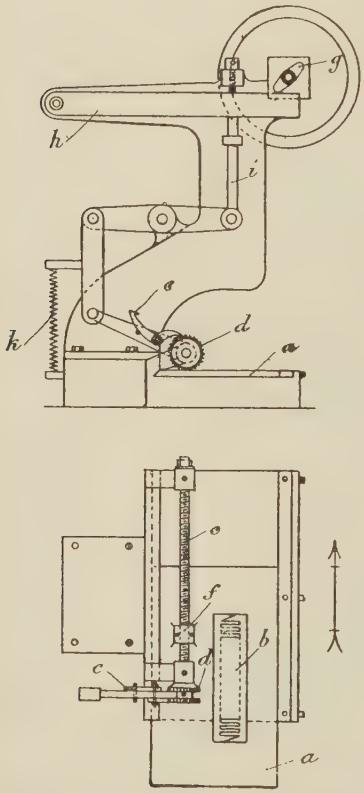


Fig. 105. Arrangement for advancing the Carriage (Meeh's Machine).

At the end of the stroke the carriage returns automatically to its place without any need for counterpoise adjustment.

The punches carrying the blades are compelled to cut into a material as hard, for example, as galalith, and cannot be arrested in their descending movement.

The great advantages of this machine are its simplicity of management and rapidity of starting, which may be brought about in less than ten minutes, while it is sometimes longer with similar machines. It only requires a small amount of power, about $\frac{1}{8}$ H.P., and may yield an output of 1000 pieces per day. The automatic throwing out of gear economises manual labour, and the same operator can superintend two machines at the same time without difficulty.

In Meeh's machine, the reversing movement is obtained by means of a special click and ratchet wheel (Fig. 105).

By the carriage *a* advancing in the direction of the arrow the piece *b* is cut, then the click *c* is raised out of the ratchet *d*; this is reversed into the opposite direction, and the click falling again controls the ratchet wheel *d*. The screw *e* is then moved in the opposite direction to the preceding, while the spring *k* moves the blades in the direction opposite to that which the lever *h*, the rod *i*, and the cam *g* would give it. (Patent 379431.)

In a general way, the regulation by screw and ratchet wheel presents the great inconvenience of requiring a change of rack each time the thickness of the teeth must be altered, thus occasioning a considerable loss of time. The ratchet wheel presents a great advantage over the screw.

In Augée's machine the adjustment of the carriage advancement is made by means of cylindrical rollers of varying diameters.

These various machines twin the combs without trimming them. The

finishing operations should therefore next be proceeded with. The following machines allow of both operations being made simultaneously, thus avoiding a large loss of time.

MACHINES FOR TWINNING AND DRESSING COMBINED.

In these machines the blades or knives are set obliquely in order to cut out sloping teeth. The rack for advancing the carriage is half a step less than the

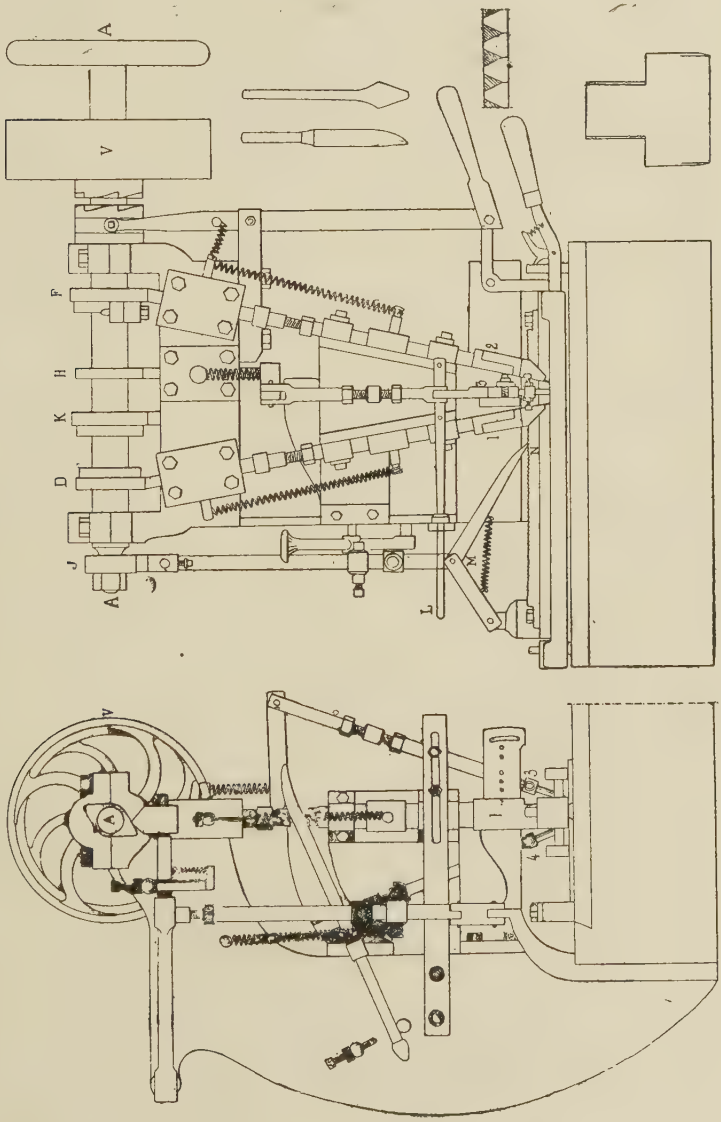


FIG. 106. Bondet's Machine.

row of teeth to be obtained, and the advancement is accordingly made in two stages. Bondet's machine works with two knives and two chisels, which perform

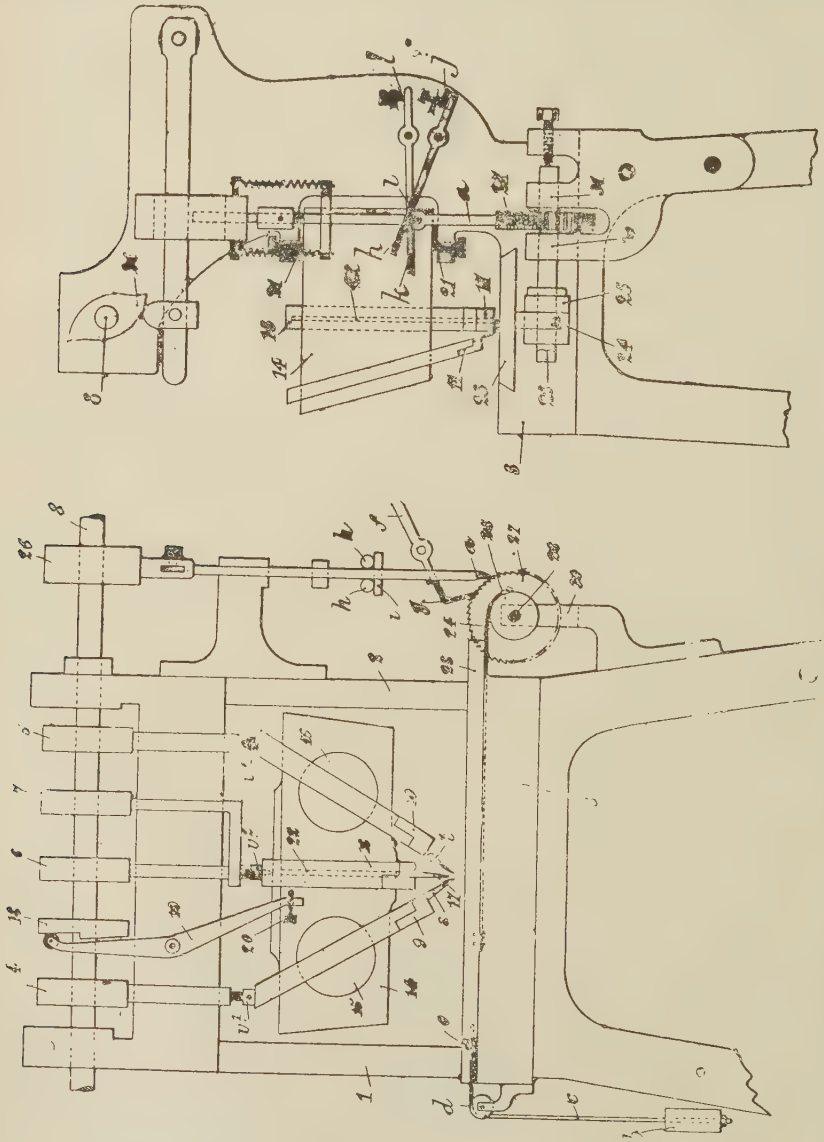


Fig. 107. Augée's Twinning Machine.

at the same time the cutting out and trimming of the tooth. They also fashion the foot of the tooth in order that the various finishing operations, such as pointing, widening, shaping, &c. (Fig. 106), may be made, and thus supplant the work of filing or trimming and also the manipulation at the mill.

The two knives 1 and 2 are moved by the cams *D* and *F*, and penetrate obliquely into the material. The two chisels 3 and 4, moved by the cam *H*, detach the teeth alternately from one side and the other.

The teeth, thus parted, are at the same time worked up by the blades 1 and 2, which remove material from the edges instead of leaving them sharp as with the preceding machines. The teeth are thus trimmed.

The dressing as made by Bondet's machine leaves a triangular waste as the shading on Fig. 106 indicates. According to the form of the teeth desired, the blades are U-shaped or not.

Further, owing to the shape of the chisels 3 and 4, which are in gouge or spear form, the base of the tooth receives mechanically and without further loss of time a shape which could only previously be obtained by hand, or at the mill, and always in a very imperfect way by pointing, widening, and shaping.

The conical form of tooth is obtained by a slow rotary movement of the principal mechanism, a movement obtained automatically by the action of the cam *K* or by hand using the lever *L* (for the first and last teeth, which must be wider than the others).

The movement propelling the plate to be twinned is obtained by the lever *M*, moved by the cam *J*, acting on the ratch *M*.

All the operations of pointing, widening and shaping may be performed with a machine of this type.

In this case the machine comprises 4 independent chisels and 4 cams. The two chisels which fashion the base of the tooth are formed of two parts.

The chisels are united two by two in V-form as indicated in Figure 108.

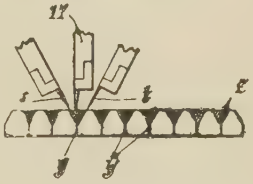


FIG. 108. Shaping by Augée's Machine.

Augée's machine (Fig. 107) for twinning and dressing combs comprises four sliding pieces regulated by the screws v_1, v_2, v_3, v_4, and worked by four eccentrics 4, 5, 6, 7, adjusted upon the shaft 8. These eccentrics transmit an up and down movement to five sliding cutter carriers 9, 10, for cutting the part to be dressed, 11 and 12 for widening or shaping, 13 for the cross section of the row of teeth.

Upon the piece 14 the two cutter heads 9 and 10 are guided by the turning plates 15 and 16, which allow of every inclination possible. The paring from the cut and the inclination of the tooth face may thus be regulated, and a tooth more or less pointed obtained.

In every case the part cut at *z* of V-form in the twin combs (Fig. 108) attains only two-thirds at the most of the thickness of the combs, so that the straight blade 17 (Fig. 107) mounted on the cutter carrier 13 in turn just separates the teeth in *y* as shown in Figure 108, giving them a properly trimmed form and not simply cut V-shaped throughout the thickness.

The shape of the tooth, seen in plan as that of a billiard cue, is obtained automatically by the eccentric 18 (Fig. 107), which gives, by means of the lever

19, a right to left movement to the piece 14 in a horizontal direction, whose amplitude is regulated at convenience by the screw 20. The five cutter carriers are guided by the piece 14, which is mounted upon two pivots 21 (Fig. 107).

A scale 22, fitted in the sliding cutter carrier 13, indicates by its descent upon the carriage at each change of blades the exact centre of the latter, which is an indispensable precaution for obtaining without rule of thumb methods a tooth of equal dimensions in both combs.

The two cutter carriers for widening 11, 12, of which only one is indicated upon Fig. 107, are worked by a single eccentric 7 (Fig. 107); they are adjustable in every position.

That which distinguishes this machine from others is the mechanism for advancing the carriage, and its adjustment for cutting coarse and fine teeth. The screw or ratch is replaced by a roller of variable diameter and easy regulation.

Upon the table 3 a carriage 23 is mounted in dovetail fashion, and receives a movement from left to right by means of a steel flexible strip 24, which rolls

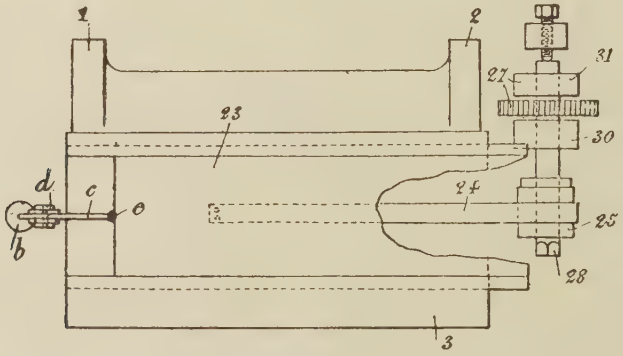


Fig. 109.

upon an interchangeable roller 25. The rotation of this roller is obtained for the period required by the eccentric 26, which acts by an advancing cam *a* upon the cog-wheel 27, fixed upon the shaft 28 and supported by the bearings 30 and 31.

To obtain a change of cut in the row of comb teeth, it suffices to place upon the shaft 28 a roller 25, whose diameter corresponds exactly to the dimensions desired for the tooth; in other words, it is the diameter of this roller which accurately regulates the advance of the carriage upon which the plate to be twinned is fixed. It follows therefore, that the dimensions of the tooth row are always proportional to the diameter of the roller employed. The steel band never folds back upon itself; from beginning to end of the winding it only occupies an arc of the roller circle.

The different rollers employed, varying in diameter according to the dimensions of the row of teeth, are easily fixed upon and removed from the shaft 28,

which carries for this purpose a fixed peg passing into an appropriate cavity provided in the rollers.

There are no pauses in the working of the machine, and a very regular cutting is obtained which favourably compares with the cutting and shaping by hand.

The return of the carriage is obtained by means of a counterpoise *b*, supported by a cord *c*, passing over a grooved pulley *d* and fixed to the carriage at *e*. After each cut it suffices to press upon the handle *f* to throw the cam of the ratchet wheel *g* out of gear, as well as to pull back the cam for advancing *a*; the carriage being thus liberated from the click and ratchet which detained it, returns automatically to its starting-point under the action of the counterpoise, ready for a fresh cutting.

For the formation of the "messelles" or end teeth, this machine possesses two levers for advancing the carriage. The first lever *h* works at a fulcrum *i*, common to both levers, upon the advancement cam *a*, which causes the carriage 23 to advance by a given length for the formation of the right-hand end teeth. In this first movement the course of the carriage is limited by the corner screw *j* (Fig. 107).

When all the ordinary teeth of the twin combs are cut, the second lever *k* acts in its turn upon the point *i* in the same way as in the preceding operation for the formation of the two left-hand end teeth; in each case, however, the stroke of this lever *k* cannot and should not be the same as that of lever *h*, and that is the cause for its regulation by a second screw *l* (Fig. 107), which secures the fit of cam *a* upon a convenient point of the toothed wheel 27.

With this double lever arrangement, the dimensions of the two end teeth of each comb are always identical. The first inner tooth on the extreme right being intimately related to the size of the cut, it is necessary for ensuring the good working of the mechanism to regulate this interval according to the dimensions required for the row of teeth. On the other hand, for the inner tooth on the extreme left an interval may be employed indifferently adjusted, since this is not related to the general working of the mechanism, thus justifying the use of two levers for the end teeth formation.

The working of the machine comprises therefore the following stages:

(1) The simultaneous cutting of the widening blades.
(2) Advancement of the carriage by the first lever *h* for the formation of the inner tooth on the extreme right.
(3) Starting the machine; advancing the carriage.
(4) Cutting by the blade *s*.
(5) Cutting by the blade *t*.
(6) Cutting by the blade 17.
(7) Further advancement of the carriage.
(8) Oscillations of the blades by the eccentric 18. Next the repetition of all the operations 1 to 8 with the exception of 2, until the ordinary teeth are all cut.

(9) Advancement of the carriage by the lever k for cutting the last inner tooth on the extreme left.

The trimming made by Augée's machine gives a V-cut as represented in Fig. 108.

Claussner's Twinning and Dressing Machine, represented in Fig. 110, may twin infant's combs, dress combs, or hairpins, from celluloid or galalith. It

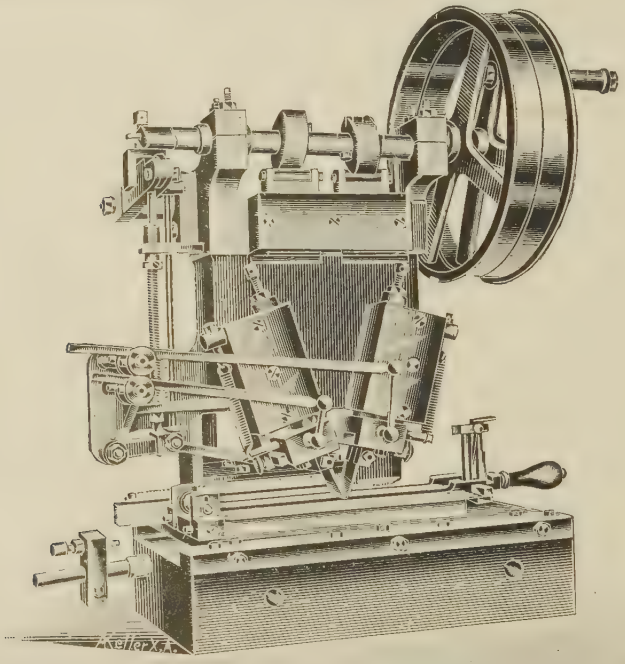


FIG. 110. Claussner's Machine for Twinning and Shaping.

works with three knives, carried by cutter heads, whose inclination is regulated by a lever system. The carriage is advanced by racks.

As in the twinning machine alone, the large extreme teeth are cut automatically. This machine is distinguished from similar ones by the fact that the three blades work simultaneously.

The machine is belt or hand driven, and requires about $\frac{1}{8}$ H.P. A slightly different arrangement of the same machine permits of making indifferently the twinning and shaping together or not. Claussner's machine trims to a V-shape similar to Bondet's apparatus.

Fig. 111, a, b, c, represents the three shapes given by the machines of Bondet, Meeh, and Augée.

These various machines cut straight combs whose teeth lengths are invariable. By a mechanism for displacing the knife carriers, certain machines permit of cutting bent combs, *i.e.* presenting in plan successive bends in opposite directions. A cutter carrier is displaced automatically in a transverse direction according to a fixed gauge, and the blades cut teeth of different lengths.

In Bondet's machine for twinning, shaping and bending, or for twinning and shaping bent combs, this movement is obtained by adapting a transverse to a longitudinal carrier. This transverse carrier is actioned by a supplementary blade working upon a beam. The carrier bears a roller which slides according to the sinuosities of a model. This carrier gives, therefore, a forward and backward movement to the twinned comb which is being made, and permits the teeth to be cut and shaped according to the varying lengths corresponding to the bend.

All the twinning machines previously described, cut out the twinned combs from flat plates. For dress combs which have a bent form it is necessary, as we have seen, to proceed to the operation of curving. This operation, carried out upon the cut out combs, possesses the inconvenience that owing to the fragile nature of the teeth there is the risk of breakage. It would seem then to be more advantageous if the curving took place before twinning, especially as the curving being made in the warm state acts unfavourably on the material, and the latter influence is worse for thin teeth than for plates.

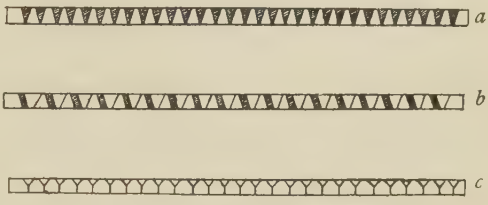


FIG. 111. Styles of Trimming.

a. Bondet and Claussner's Style.
b. Meeh's Shape. *c*. Augée's Form.

The following machine, recently patented by M. Convert (Figs. 112 and 113), is for the purpose of twinning plates previously curved, in such a way that the comb emerges from the twinning machine with its definite form and outline.

The machine comprises: a frame *a*, carrying two bearings *b* (Fig. 112), upon which turns a shaft 1, provided with fixed and free pulleys 16, 17, and two plates 2 and 3, supported at 180 degrees with reference to each other, so as to produce alternately depressions of the blocks 5 and 6. These blocks carry the twinning blades 7 and 8. Two catch-springs, 14 and 15, promote the re-ascent of the cutter heads 5 and 6.

The horizontal carriage of existing machines is replaced in this new arrangement by a drum 10, mounted on an axle *b*, carried by the frame *a*. The axle *b* is situated in a plane perpendicular to 1, and forming the median plane of the angle between the two blades 7 and 8.

Upon 10 is fixed a ratchet wheel 11, between whose teeth operates a catch 9, by the spring *c*, pivoted at *d* to the frame *a*.

The double plate 4, supported upon 1, operates on the head of a bar 12, suitably directed and jointed at *e* to the catch, so that when depressed the

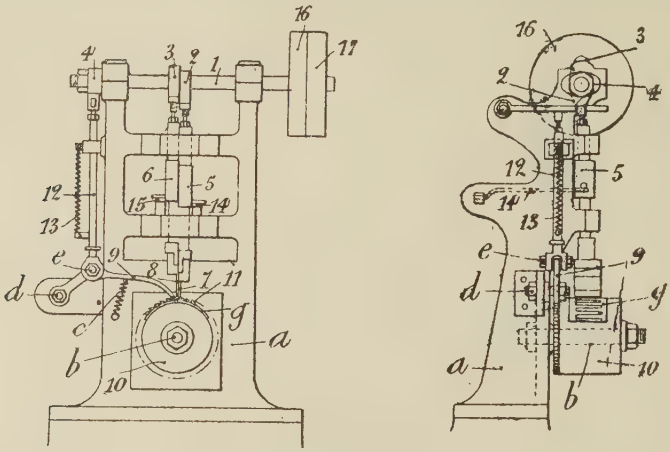


FIG. 112. Convert's Twinning Machine.

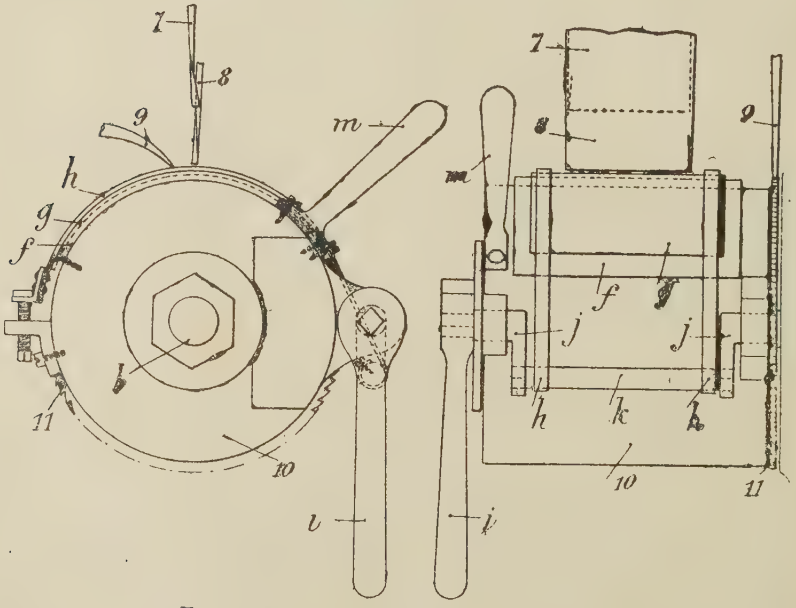


FIG. 113. The Drum of Convert's Machine.

rod 12 pushes the catch 9, which is between two teeth of the ratchet wheel 11, and causes this to be displaced by a tooth.

When 4 has ceased to act, a spring 13 raises the bar 12 again, and the catch 9 just falls between the next teeth.

Upon the drum 10 is arranged a frame *f* (Fig. 113), upon which is placed

the plate to be trimmed, g; the external surface of the frame fits the concave surface of the plate. Flexible bands h press upon the edges of the plate g and maintain it in position. These bands are stretched by turning a shaft $j\ kj$ by means of the handle i.

During a semi-rotation of the axle 1, one of the plates 2 for example, lowers the block 5, the blade r traverses the celluloid plate g, then the spring 14 raises the block 5 and the blade 7.

During the succeeding semi-rotation the same procedure is undergone by the plate 3, the block 6, and the blade 8. When one of the blades, that which just cuts g, remounts, the double plate 4 operates, and the drum 10 advances by a tooth before the other blade touches the plate. When a twinned plate has been removed, the handle m permits the drum to be returned to its starting-point.

This system of ratchet drum may be adapted to every type of existing twinning machine (for shaping or bending).

This machine has been quite recently patented, but we do not know whether it has been utilised industrially, nor yet the results afforded by it. It is interesting, however, to notice such research in fresh directions.

In what precedes we believe we have given a good account of the twinning process, of the rapid progress accomplished in this direction, and the actual state of the industry.

If comb twinning has been, and is yet, the object of much attention, moulding has not attracted less attention industrially, because it is obvious that an efficient moulding process would permit of cheaper comb production.

THE MOULDING OF COMBS.

Moulding is hardly employed other than for ordinary cheap combs such as the large hair comb, since, up to the present, it has only afforded mediocre results as regards finish and cost.

The mediocrity of the results lies in the fact that if freshly prepared celluloid blocks be employed direct from the press, porous plates are obtained through the volatilisation of the solvent in contact with the hot walls of the mould. If, on the other hand, we proceed as in ordinary moulding, by employing dry plates to which the requisite plasticity has been imparted by heat, immersion in boiling water for example, a more satisfactory result is not obtained. Indeed, the effects of tension and displacement of the material are such that the moulded comb may crack and rend, and the teeth break off during drying.

The properties of the material employed are profoundly altered by stamping or moulding; the projecting parts of the moulds penetrate into the substance like blades, and their approach produces a rolling effect. There is therefore produced an intense working up of the material, which destroys its quality and alters the tints. The fairly frequent renewal of the moulds, and the proportion of defective pieces, considerably augment the cost price, thus reducing the

economy effected by moulding over twinning. In addition burrs are always produced which must be afterwards removed, thus necessitating expensive work.

The Rheinische Gummi und Celluloïd Fabrik, of Neckarau (Mannheim), employ some interesting processes, which obviate the defect of tearing, but they have the disadvantage of requiring a certain amount of skill. The celluloid must also be of a particular quality and perfectly homogeneous.

The moulding in this process is made in two phases, for avoiding too great molecular strain. In the first phase a block or plate is cut up into sheets possessing the contour of the comb with bevelled section, or this sheet is produced by forcing pasty celluloid through an aperture possessing the bevelled section of the comb. This sheet of great length is next cut up into sections, each having the length of a comb. In this operation the celluloid is not submitted to any molecular tension, and no tearing is produced.

The second phase consists in giving the comb shape to the plate obtained in the first phase. For that purpose the warm plate is pressed into a matrice. In this second operation the celluloid plate is not submitted to very appreciable molecular strain, the pressures being reduced to a minimum and distributed as uniformly as possible, on account of the differences in thickness of the plate which possesses the same sloping section as the comb. Therefore there are no greater pressure strains in the tapered portion of the finished comb than at the back, and these strains are uniformly distributed. The deformation is the same everywhere, and there is no fear of breaking. The definite tooth shape is given without the expensive work of trimming being necessary, and the comb has only to be cleaned and polished.

The chief point is that the celluloid plate submitted to compression has dimensions harmonious with the piece to be obtained, and therefore every inequality of appreciable molecular tension should be avoided during compression to prevent any molecular rupture during this operation.

This kind of work is more expensive and delicate than ordinary moulding, and hardly presents any advantage over twinning.

In order to diminish the delicacy of the first operation, and avoid also any chances of rupture, the Rheinische Gummi und Celluloïd Fabrik has modified this process by pressing the celluloid into the hollow of the matrice instead of stamping out the comb

It is hardly necessary that the plate should be previously brought into a shape corresponding to the section of the comb, and it suffices that its volume should approximately correspond to that of the finished comb, so that during moulding the hollows may be entirely filled. A length and thickness are therefore given to the plate nearly equal to that of the back of the comb, so that during the passage from the initial form to the final no great rupture strains will be introduced.

This process of pressing the material into the mould has been much further extended by the Rheinische Gummi und Celluloïd Fabrik, which has converted

it into a veritable rolling operation (Patent 339685, 1904) A piece of celluloid is taken having nearly the same length and thickness as the final product. This piece is introduced into the matrice, so that the back presses tight to the back of the matrice with a reserve of material. The piece has a width inferior to the length of the teeth so that the channels of the mould corresponding to the teeth are only partially covered by celluloid. By pressure the celluloid is

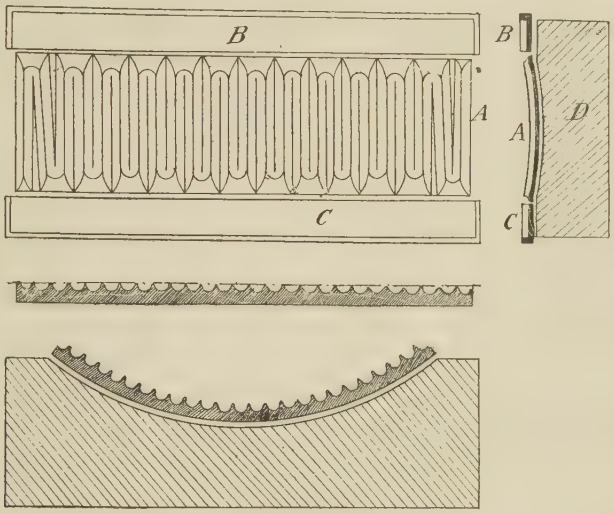


FIG. 114. Bondet's Mould.

forced to the interior of the mould forming the back of the comb and teeth as long as the mould channels.

The reserve of celluloid is thus forced towards the extremities, and under these conditions the celluloid, instead of being torn, penetrates into the channels, thereby augmenting the density. For double combs, known as small-toothed combs or dust combs, the reserve of celluloid should be placed at the middle of the outline; for ordinary combs, or large hair combs, it should be placed at the back of the comb.

The process patented by Bondet consists in employing metal moulds of curved shape, formed by an assembly of thin plates upon a solid support, as represented in Figure 114.

We have described in another place the processes for moulding celluloid by Lamy-Bellignite, Alambert-Bondivenne, and Dérobert which may be applied especially to combs. These processes are all a trifle delicate for moulding operations. They appear, moreover, to necessitate a celluloid of particular plasticity.

The following process was patented by La Société Anonyme Petitcollin (Patent 361710) with the object of remedying defects which result in the

matrices or moulds, these being especially at the ridges, which blunt rapidly and break under the enormous pressures. It has the additional purpose of bringing accurately together the two matrices so as to avoid burrs or seams.

The principle is the use of moulds previously closed at any pressure upon the material, and it necessitates a special press. A piece of material of weight slightly superior to that of the object desired is enclosed in a hollow mould, whose interior has the shape of the object to be obtained, and is arranged in such a way that, while preserving its tightness, the internal volume may be gradually reduced to the point where it attains that of the material introduced; the moulding is then effected.

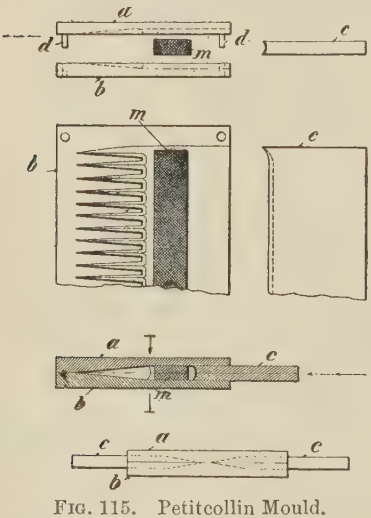


Fig. 115. Petitcollin Mould.

Moreover, the volume variations of the mould are made in such a way that the material is prevented from being displaced towards the containing walls.

In this way the ridges of the mould forming the line of demarcation of the teeth do not undergo any kind of appreciable straining capable of blunting them (the material moving parallel to the ridges), and therefore retain their original rectitude. The pressure supported by the mould is the same in every case, since this pressure has not to be increased for the expulsion of hard material interposed between the impressions. It suffices to give the mould dimensions in accordance with the pressure adopted so as to avoid any breakage. By this moulding process the material does not undergo division followed by re-welding, which would alter the quality and mix the colours. Finally, the operation being conducted in a closed vessel, there is no risk of the material losing certain of its constituents by evaporation, and consequently its principal properties do not change. The latter is a very important point for celluloid.

The mould having a variable internal volume, every error in the weight of the material introduced is without effect on the correctness of the object obtained. Waste from want of material is avoided, and should some pieces present defects it is possible to remedy these by subjecting to a fresh pressing in the mould. Finally, and most important, the pieces emerge from the mould completely finished. All parts of the mould form a single piece, there being no median seam formed between the teeth, and therefore the operation removing the seam is dispensed with.

The mould adopted in practice is in three pieces, two matrices *a b* fixed during the operation, and a piece *c* forming a movable wall which embeds itself by friction into the matrices to modify the internal volume of the mould and compel the material to take up its shape (Fig. 115).

The matrices *a b* constitute the mould proper. These are accurately dressed and regulated, one upon the other, either by the centre pins *d* or by any other mode of accurate adjustment, so that their casts, which represent in mould the piece to be obtained, coincide perfectly.

At the right side of the back of the comb these pieces are grooved so that when superposed they allow a passage of rectangular section into which the third piece *c* exactly fits. This piece slides with little friction in its bed, hermetically closes the mould, and by its displacement varies the internal capacity.

The inner face of this piece *c*, which is perpendicular to the direction of movement, is cut conveniently according to the shape desired for the comb back.

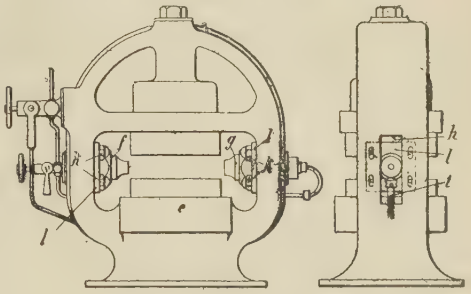


FIG. 116. Petitcollin Press.

The principal pieces *a* and *b* are suitably pierced with internal passages, not represented in the figure, into which steam, cold water, or any other suitable liquid may be injected, permitting of either rapid heating or cooling.

In practice, two of these moulds cut from the same piece of metal are paired back to back (Fig. 115).

These moulds are utilised in combination with a special hydraulic press (Fig. 116), which contains a vertical plunger *e* of great diameter capable of pressing strongly a horizontal plate accurately dressed against a top piece which is perfectly parallel with it.

Two small presses *f g* with horizontal plungers are arranged laterally. The axes of these two small plungers coincide; they are in the plane of the large plunger axis and perpendicular to it. The position of the horizontal axis of the small plungers is variable in height. For the latter purpose the small horizontal cylinders *f g* slide vertically, each in a groove *h* contrived in the press cheeks; they rest upon a regulating screw *i* which determines their height, and they are fixed at the place desired by the four pins *k* which lock their square flange *l* upon the inner plane face of the cheeks.

Suitable fittings give the large piston an action independent of the small, and do not allow the latter to operate until after the large piston has attained its position. This is to avoid any deterioration of the moulds by bad management.

The working of the press is as follows:

The chosen mould is introduced in front of a press whose plungers are slack. The material *m* being introduced by the opening which allows the withdrawal of the movable pieces *c*, the mould is closed by replacing the latter, and then steam turned on. The mould is next glided into position between the plates of the large vertical plunger. This having been tightened, the two small pistons are set in motion, which, simultaneously and symmetrically, drive the pieces *c*

towards the interior of the mould. When this movement has ceased the moulding is at an end.

Keeping the whole under pressure, cold water is turned on; then the pressure is released and the mould removed for another operation.

The shape of the mould, as well as the arrangement of the movable wall, varies according to the form of the combs to be obtained.

Such are the various moulding presses which have been tried for the comb manufacture. In reality the combs obtained are never as durable as those obtained by twinning. It should not be forgotten, moreover, that every operation involving heating and pressure profoundly alters the material.

PROCESS OF COMBINED TWINNING AND STAMPING.

The following process, recommended by the Convert Company, has for its object the avoiding of defective homogeneity which results by the pressing of certain parts of the plate during the stamping. The excess material at certain points undergoes in reality over-pressure by displacement of the celluloid, and there results defective homogeneity and durability.

In this process two combs are stamped out at a time, as in the stamping by means of two semi-matrices, which present alternately punches and hollows, the punches of one matrice being opposite to the hollows of the other. Each punch possesses sharp edges between which is a concavity for holding the strips of material cut by the sharp edges. When the two matrices approach the celluloid plate is cut, and the punches of the one matrice just come between those of the other pushing the cut material before them.

The operation is in reality a combination of cutting and moulding or stamping. The cutting is completed before the stamping commences. The latter is performed upon the cut strips which are no longer connected with the neighbouring portions, thus facilitating the division of the material and avoiding surplus pressures.

The following Figures exhibit the operation in the different phases. Figure 117*a* before stamping, Figure 117*b* the end of twinning and commencement of stamping, and Figure 117*c* the termination of the stamping.

Each of the matrices consists of a plate *A*, *B*, carrying a series of projecting punches *a*, *a'* alternating with hollows *b*, *b'*, the punches *a*, *a'* corresponding to the hollows *b*, *b'* and *vice versâ*. Each of the punches possesses sharp edges *c*, *d*, between which are the spaces *c e d*. The hollow *b* between each punch has naturally a depth equal to the projection of the punch (if the teeth are triangular as in the case of the Figures).

The back of the combs is limited by the cutting out of the plate *M* by means of the sharp edges *I* and *J* (Fig. 118). The plates *V* and *S* can receive at convenience a circulation of hot water or steam for softening the celluloid, or one of cold water for removing the mould.

The great drawbacks to stamping are the formation of burrs at the joints of

the matrices and the curving of the combs. With the object of remedying the latter inconvenience, M. Convert recommends stamping with matrices having the curvature of the comb to be obtained. These two matrices cut from the

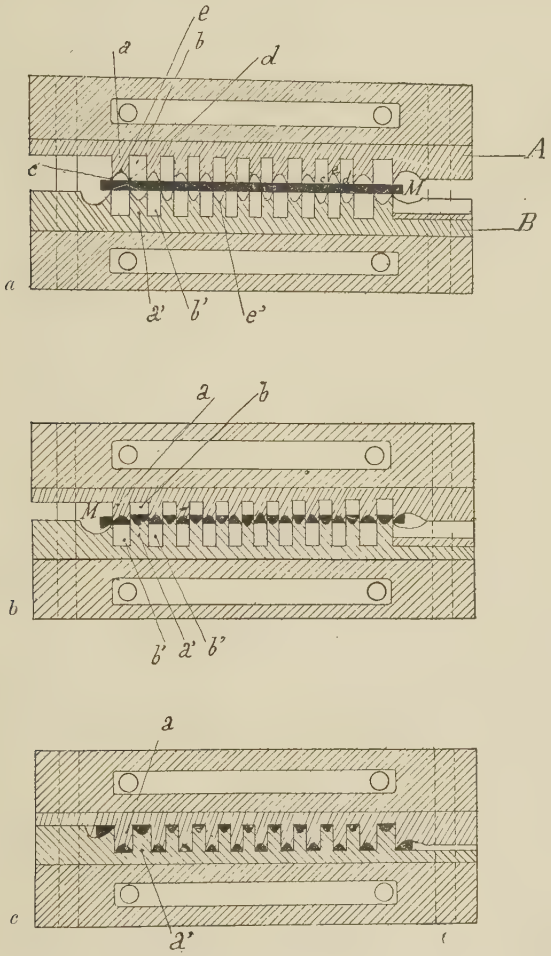


Fig. 117. The Convert Process.

celluloid a plate having the requisite comb contour. The combs are then placed in the position they would have if they had emerged from twinning.

When the matrices meet under the influence of pressure and detach the contour of the plate, the projecting parts of both matrices are still about 1 millimetre apart, so that the stamping is produced almost at the same time as the plate.

The plate is then withdrawn from the mould, and the portions in the hollows,

which should be detached from the object, are cut away. A comb is thus obtained without burrs (Patent 390324). This process appears a trifle complicated.

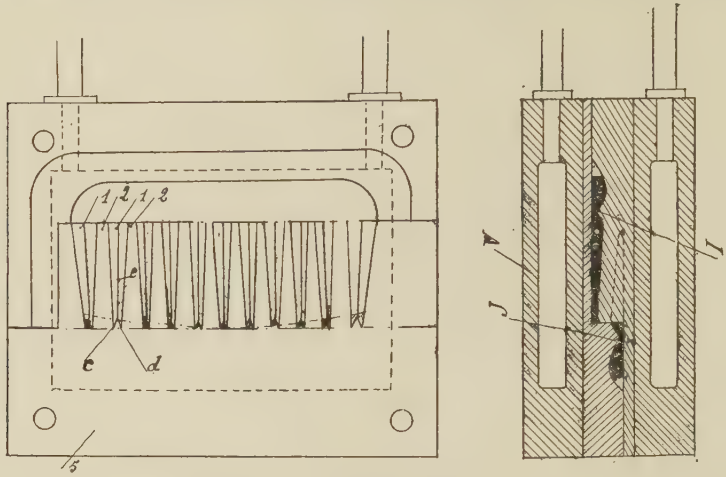


Fig. 118. The Convert Process.

INSTALLATION OF WORKSHOPS FOR THE MANUFACTURE OF COMBS.

Comb working presents certain dangers as much from the hygienic standpoint as from fire, and these dangers render necessary certain arrangements of the workshops and certain precautionary measures.

From the hygienic standpoint the dust, which is formed in considerable quantity during comb manufacture, constitutes a real danger. This dust is formed particularly in the engraving shops. The parings detached at the mill have received from the workmen the name of "cornaille," a term preserved from the older horn comb industry. These parings fall upon the work table or are projected against a board placed behind the milling cutter. The celluloid dust is cast up into the air around the operator, whose mucuous membrane it speedily attacks, while it constitutes a perpetual danger of fire.

The operation known under the name of "tournage," or discharging the rollers, also gives rise to the formation of a large volume of dust, containing fragments of cloth and pumice powder. To-day this operation is usually performed outside the buildings.

The passage through acetic acid gives rise to the disengagement of unhealthy fumes.

Finally, the great inflammability of the material employed and the charging of the atmosphere with celluloid dust, inflammable to a high degree, renders the danger of fire very great. The workshops most exposed to danger are those for working at the milling cutter, this tool frequently producing sparks which may inflame the parings or dust.

For these various reasons the workshops should be arranged in accordance with the following principles:

The workshops should be as distinct and separate from each other as possible, and for preference on the ground level. This arrangement has the double advantage of reducing the accumulation of inflammable material in one set of

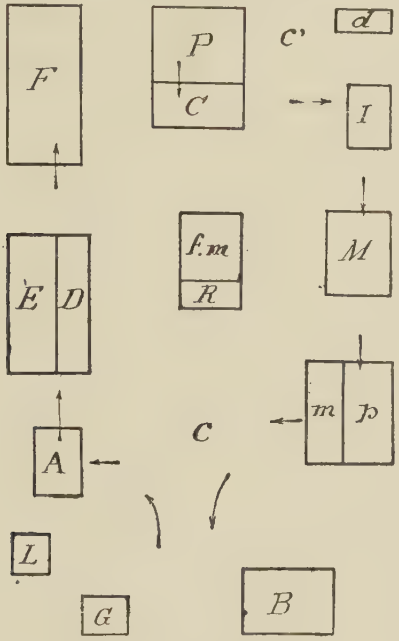


FIG. 119. Arrangement of the Workshops in a Comb Factory.

ITEMS.

B. Office.	*I.* Acid Treatment.
G. Works Caretaker.	*M.* Mounting and Ornamentation.
L. Laboratory.	*p.* Bending.
A. Stores.	*m.* Store.
D. Cutting up and Tapering.	*fm.* Power and Hot Water generating House.
E. Twinning.	*R.* Repairing Shops.
F. Shaping, Engraving, Bordering, &c.	*d.* Waste.
P. Pumicing.	*c.* Yard.
C. Curving.	*c'.* Yard for Cleaning out the Rollers.

premises, and of facilitating its removal. On the other hand, in case of fire at one of the workshops the encroachment of the combustion or decomposition gases into the neighbouring workshops is avoided.

In a comb works an arrangement similar to that indicated in Fig. 119 may be adopted with security, this being applicable to a works in which the raw material is not itself produced. The partition is carried out to a sufficient degree without entailing the construction of too many buildings. The workshops connected should be separated by a thick wall, and the buildings sufficiently

interspaced. The shaping workshop has been considered the most dangerous from the fire standpoint, on account of the sparks produced by the machinery. This has been isolated. The offices are completely isolated from the workshops and stores, and can be allowed another floor. The course followed by the material during manufacture is regulated so as to involve no return, and therefore no loss of time. The transport from one workshop to another is naturally made by mechanical means, and this will be the more efficacious as the arrangement of the workshops assures a rational carrying forward of the material. The power house has been placed nearly at the centre of the positions of those workshops which require it.

The waste is with advantage thrown into closed sheet-iron tanks, which should be emptied each day into a shed or well-ventilated and isolated premises. This waste is resold at the rate of 0·40 to 0·60 francs per kilogramme for a treatment already mentioned, or is utilised in the same works, should this manufacture its own raw material.

Near the pumice polishing shop an open space has been provided in order to clean out the pouncing rollers. This operation consists in removing the cloth fragments, which in time exceed the others, by means of a very sharp blade, during which the roller revolves at great speed. The operation produces a large amount of dust, containing cloth fibres and pumice powder, and is, therefore, advantageously performed outside. Certain firms employ grinding and polishing machines, which avoid rollers and their cleansing.

The passage through acid is also made as far as possible outside, on account of the evolution of acid fumes. In winter this operation must be done inside; there must, therefore, be thorough ventilation. A stove surmounted by a hood is often placed in the middle of a workshop with defective ventilation, in order to promote a draught. This appears inadequate to us. In every case the hood should be surmounted by a chimney sufficient for ensuring a powerful draught. Stove-heating constitutes a danger, and should be replaced in all workshops where celluloid is manipulated by steam or hot-water heating.

In many shaping workshops (for engraving, fluting, &c.) the following arrangement is adopted against dust. The bench bottom is enclosed by a removable glass or mica plate, which is prolonged above the tool. This plate is provided with two lateral plates and a movable face of mica or glass arriving as far as the milling cutter. The work is, therefore, carried out in a semi-glass cage, and the operator is partially sheltered from the dust, which cannot be deposited on any part but the bench. A dust aspirating system would evidently be preferable, but the above arrangement is already a wise precaution.

Against each bench a zinc or sheet iron bath is fixed filled with water, into which the operator drives the dust from time to time.

When taking all the precautionary measures mentioned in the chapter dealing with the inflammability of celluloid, it will be remembered that electric lighting was considered the safest form of illumination. The most convenient mode of power transmission is also electric. As pointed out on the subject

of hydro-extractors, motors are constructed which do not spark at the brushes whoever superintends them; nevertheless the motors should be protected.

Organisation of the work at Oyonnax. We shall terminate this study by indicating briefly the works conditions at Oyonnax, which is the greatest comb-producing centre, and whose organisation is at the same time peculiar.

The majority of the Oyonnax population are employed at the comb works. The men carry out the twinning, pumice polishing, and shaping. The women do the curving, polishing, acid treatment, bending, and certain shaping operations. Children engage in the acid treatment, bending, mounting, and certain shaping operations.

For the latter, which comprise filing, engraving, &c., each operator has his speciality.

What specially characterises the Oyonnax industry is the existence of few factories, the work being done mainly in families. There exists, in consequence, alongside the huge factories of La Société Industrielle de Celluloïd, L'Oyonnaxienne, and L'Oyonnithe, a multitude of small workshops. The comb manufacturers furnish the small makers, or the families who perform only one or more of the comb-making operations, with raw material, similar to the practice in Vimeux, for example, in the lock trade. A number of dwellings comprise, in consequence, alongside the living house, a small workshop in the garden where the various operations of comb manufacture are carried out.

For work which necessitates motive power there exists at Oyonnax a certain number of stations for supplying power, some of considerable size.

Besides motive power the power firm, known locally as "le tournant," supplies the workshops or cabinets with benches and lighting. The tenant, workman, or small manufacturer employing a few workmen supply the tools.

Since the development of electricity, many workmen and small manufacturers have abandoned works with motive power for electrical power at home, and this has further contributed to the diffusion of the family work system. The Oyonnax workmen have been comb makers from father to son for many generations, working with horn previous to celluloid; they have, on this account, acquired a skill and style which permit them to maintain the great reputation of their industry. This system of organisation has also contributed to attach the workman to his native soil, at least until recent years.

We imagine, on the other hand, that the principles enunciated by us on the installation of workshops are only applicable to factories proper where the whole cycle of operations, from detailing to mounting, are carried out; and that on account of the division of work the principles are scarcely put into practice in other workshops. In the case of home work only small inconveniences are entailed, but with motive power firms, which let out the cabinets, this is no longer so, since the workshop separation no longer exists.

CHAPTER III

THE HANDLES OF STICKS AND UMBRELLAS

Celluloid is used for imitating horn, ivory, meerschaum, amber, coral, pearl and wood for the handles of sticks and umbrellas.

The ease with which it is stained, its brilliance, relative permanence and strength, plasticity to heat, and finally its cheapness, render the substance invaluable for this manufacture. It is less fragile than meerschaum, ivory, tortoise-shell or pearl, and is ornamented more readily. It is even preferable to wood, whose varnish rapidly wears off, and whose fibres, for handles curved by heat, break and detach. It deteriorates less than horn. Handles may thus be manufactured, straight or curved, plain or decorated, imitating the heads or bodies of animals or other subjects, and either hollow or solid.

In Germany, according to Andès, more than 4000 dozen per annum of most varied design are manufactured.[1]

In France many more are manufactured, especially for export. There exists a prejudice against celluloid, on account of the strongly exaggerated dangers of fire, which have caused it to be rather shunned by French tradesmen. Its cheapness, however, makes it preferable to the much more costly articles known in France by the term "de luxe." We have seen very pretty celluloid effects, affording perfect imitations, by the firm of Hemmen at Lilas near Paris.

For this kind of work celluloid is used in sheets, plates, rods or tubes according to the species of handle, and manipulated by the three different processes of moulding, blowing or drawing, according to the shape required. Handles manufactured from sheets are made by moulding followed by welding. Hollow handles are made by blowing or by moulding and welding, according to the nature of the handle.

This work necessitates moulds or forms, presses and steam injectors.

BLOWING.

The blowing is made by means of celluloid tubes. The tube is placed in a mould which possesses as a hollow cast exactly the design we wish to produce upon the exterior of the handle. These moulds are made of two parts for the easy introduction of the tube, the parts being exactly adjustable to each other, the latter being an essential condition since the closing should be air-tight. The two extremities of the mould are terminated conically, and carry seven threads, which permit the two parts to be tightened to each other, at one side by a closing plug and at the other by a tubular cone. Both allow the two parts to be adjusted, all being easily removed.

[1] Louis Edgar Andès, "Zelluloïd und Seine Verarbeitung," 1908.

The celluloid tube is placed in the mould, which is then closed and placed in communication with steam. The latter passes into the tube, softens it, and at the same time applies it to the mould walls, whose form it takes. After withdrawal it is chilled by immersion in cold water.

This process is well adapted for simple handles whereby only a celluloid tube needs to be enlarged. Certain firms advantageously give a preliminary heating to the tube by steeping it in boiling water. In this case the tube is occupied for preference by a caoutchouc core, which expands in the hot water and enlarges the tube without deforming it. The core is then withdrawn and the tube quickly placed in the mould.

At present the mould is usually closed by pressure. The mould is placed upon the plate of a screw or hydraulic press, whose head carries another plate facing the lower. The mould is tightened between the two plates, and this pressure assures a more efficient closing than by any other arrangement providing the two sections of the mould are perfectly plane and adjustable. This process very much simplifies the operation.

When the handles have been obtained in the preceding way by tube enlargement the ends are open. The upper extremity is closed by a celluloid sheet cut into a cap and welded to the tubular handle generally in conical form. The welding is made by acetone, a substance which has the property of softening celluloid and so permitting of its being welded. The edges for welding are soaked in acetone, applied firmly to each other and allowed to dry for several days.

It only remains to trim the piece, *i.e.* to smooth out the parts which have been softened, and to remove the burrs or swellings which always result from pressing against the joints of the mould whatever the mode of adjustment. This trimming is performed by a scraper, following by cleaning at a disc machine similar to those used for pumice polishing. Finally the polishing and decorating are carried out if required.

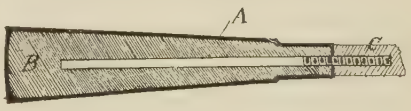


FIG. 120.

The hollow handles are fixed to the cane or stick of an umbrella by means of plaster, but care should be exercised in employing very good plaster and of allowing for careful drying. A special cement is to be preferred.

These handles are not usually left hollow. They are filled with fine plaster, conforming to the precautions indicated previously, these being essential for strength. The plaster is only used for opaque celluloid handles and ivory imitations. Plaster may be replaced by colophony, which may be stained better in all shades and which may be recovered with opaque or transparent celluloid.

The handle is made firm by introducing a wooden rod into it (Fig. 120). The handle is thus made up of a celluloid casing *A*, a filling of plaster or

colophony *B*, and a rod for rigidity *C* of wood or metal which should naturally not entirely fill up the internal space of the handle. This rod carries at its extremity a screw thread on which the stick or umbrella may be screwed. A more simple process consists in making the rod *C* part of the umbrella.

The method of blowing described above is carried out with ordinary steam. Recourse may be had to the use of dry steam, which facilitates welding by avoiding moisture in the celluloid. Compressed air may also be used. The technique presents nothing in particular as regards stick and umbrella handles, and the general procedure is utilised for the manufacture of hollow articles. The finishing is the same as in the preceding processes.

Certain German manufacturers employ for the manufacture of these handles a process which permits of making two pieces at a time, similar to that for combs and known as the "Doublierverfahren." The difference lies merely in the constitution of the mould, which is double and allows of two pieces being made together.

Fancy handles. Fancy handles imitating various subjects of uneven shapes, such as the heads or bodies of animals, may also be made by blowing tubes. In this case never more than one at a time is made. The tube is placed in a mould of two sections, having an aperture for the admission of steam, and whose interior is shaped according to the shapes to be given. The thickness of the mould walls should naturally be greater than the above.

The course of the operations is identical.

MOULDING.

Hollow handles. All the preceding shapes may be obtained by moulding, employing moulds in two sections as previously but without a blowing neck. A core formed of several sections is introduced, which may be removed at the end of the moulding process. Most usually, however, blowing is used, and moulding is hardly employed other than for handles and knobs welded in two pieces or for massive handles.

Massive handles. These are moulded from a celluloid block soaked in boiling water, which is then placed in the mould and submitted to a press compression either by screw or hand wheels, or in a hydraulic press.

The moulds are mostly of red copper, closed at both extremities, and previously warmed upon heated plates. The pressure is allowed to be continuously exerted until the second mould is ready for placing under the press.

To facilitate the removal of the mould the latter, before moulding, is passed through soap water to expel the adhering celluloid.

Handles in two pieces. The moulding is usually made by employing two celluloid plates which are moulded and then welded.

This operation is very simple, and is applied especially to handles bent at right angles, to fancy handles, and also to those imitating finely veined ivory.

For the latter, tube-blowing does not give good results, since the distending of the tube in the blowing process deforms the veins in the celluloid.

The two plates are previously sawn to the desired dimensions, then softened in boiling water and next placed in moulds comprised of a hollow part and a corresponding return portion forming a core. The moulds are preliminarily heated by passing steam into the moulds or by hot plates, and pressure is applied as in the preceding process, exercising the same precautions in view of the mould's removal.

The moulded plates are removed and placed to dry, then the edges are trimmed with a smooth file, and the two parts welded by acetone.

The trimming, cleaning, polishing and decorating processes are then performed according to requirements.

Twisted hollow handles. Handles bent many times upon themselves are obtained from tubes by a caoutchouc mould. A core consisting of a spiral of flexible caoutchouc is introduced into the interior of a tube, and the whole placed in boiling water. The caoutchouc expands under the influence of the moist heat, while the celluloid softens and at the same time assumes the shape and diameter of the caoutchouc upon which it is tightened. While the celluloid is in the plastic state it is bent to the shape desired. After allowing to cool a short time the caoutchouc core is withdrawn, so that the celluloid may become rigid and retain its shape; the caoutchouc, by virtue of its elasticity, expands lengthwise, while its diameter contracts, under a stretching force, and is thus easily withdrawn. The handle is then placed in cold water and the celluloid becomes hard. The extremity is closed by an acetone welding.

THE DRAWING PROCESS.

Handles placed upon wooden cores. This kind of work differs entirely from the preceding; it permits of covering the curved handle of a stick or umbrella with a celluloid tube imitating wood, horn, tortoise-shell, ivory, &c.

For this purpose a special apparatus is used, formed of a flat plate of red copper, terminated in a point at one of its extremities. On two sides of this plate is a groove in which are placed very small rollers capable of rotating on their axes. This plate is put into a celluloid tube, and the whole placed into boiling water where it is subjected to a backward and forward movement. The tube is enlarged by this motion. It is then withdrawn from the water and drawn upon a wooden core forming the handle, which it is made to exceed in length by about two centimetres. On cooling, the tube contracts and is compressed upon the wood. The end is then tied so that the edges may be softened and fashioned to a point, after which it is cooled with water, the part beyond the knot cut off, and the end neatly finished off.

A very different process from all the preceding ones may be employed for the manufacture of hollow twisted handles. According to Andès, it should effect an economy in material, permit of manufacturing two handles at a time,

and preserve more easily the shape desired for the handle. It consists in first forming a conical tube and afterwards curving it to the shape desired.

A tube is taken and cut obliquely into halves, so as to form a prolonged slope, as represented in Fig. 121. The slope is worked to a point by softening with warm water and pressing the extremity of the tube upon a pointed steel core. The two edges of the cut brought together by the conical formation are then softened with acetone. The tube is next curved according to the shape desired.

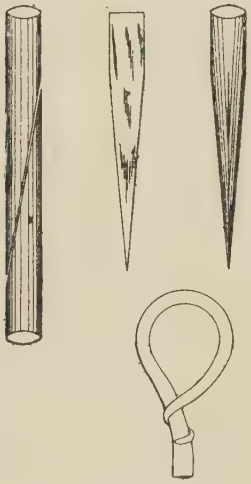


Fig. 121.

In reality this process appears to us to demand more complicated manual labour than caoutchouc curving, which is a set-off against the small economy of primary material.

Celluloid may also be employed for handles simply as a protection for another fragile substance or as a support to a substance deficient in rigidity.

For example, pearl, which is very fragile, may be covered by a sheet or very thin tube of transparent celluloid. The above is the process of Alphonse Ludwig and Co.

VARIOUS KINDS OF HANDLE.

The preceding processes are naturally applicable to all kinds of handles; handles of bicycles, of children's carriages, imitating porcelain, of mattocks and doors. By these processes very beautiful porcelain imitations are obtained, which are not brittle and accordingly not fragile. Enamelled handles are also imitated, by employing two transparent celluloid sheets to which a sheet of paper or metal is fastened bearing the designs to be represented. The two sheets brought to the shape desired, and upon which has been fastened the design required, are welded, and a perfect imitation of enamel obtained.

Decoration. The decoration of celluloid handles by incrustation was formerly made only on celluloid placed on cores; modern processes permit of making it upon softened celluloid without recourse to rigid cores.

These processes will be discussed in the article on "Decoration: Incrustations, &c."

BICYCLE HANDLES.

The handles for bicycles are made according to preceding methods in addition to a filling material.

The following filling process is due to Dr. Hunœus of Linden (near Hanover).

Into the handle *c* a tube *d* is introduced corresponding to the internal diameter of the handle extremities, so that these may be fastened upon it. This rigid tube is pierced with apertures *e* in its central part (Fig. 122). There is then introduced into it a plastic substance, which hardens on drying, *e.g.* a thick

paste of sawdust and glue, which is compressed into the tube possessing a closing partition *h*.

By compression, the material penetrates into the holes and runs over from the tube into the median part *b* between this and the handle. The shape of the handle therefore is unmodified by the pressure of this material; by the extremity

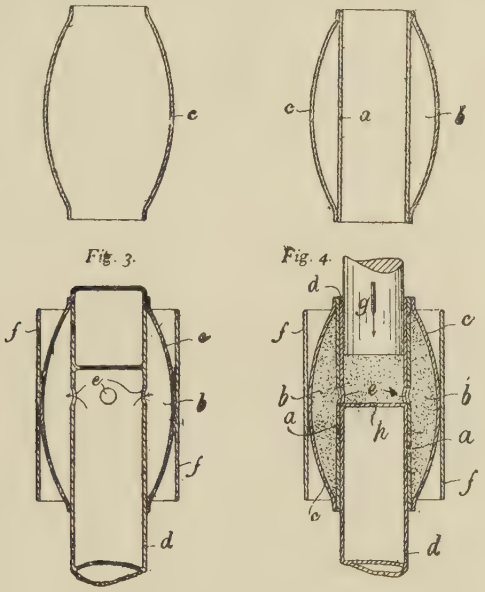


Fig. 122. Bicycle Handles.

of the tube a large envelope *f* is fixed, which slips over the handle when the tube is glided to the interior. The paste of sawdust and glue may be replaced by plaster. An envelope of paste *a* is placed in the tube, and this layer when hard is pierced with apertures corresponding to the holes of the tube. As before, the tube with its case is introduced into the handle and at the same time the previous envelope is glided upon the handle. The tube is filled with paste, and this by pressure is forced to pass, as before, between the handle and the tube; the latter is then withdrawn, and the material remains between the handle and the envelope of hardened paste, where it dries and so becomes hard.

CHAPTER IV

THE MANUFACTURE OF HOLLOW ARTICLES

GENERAL INFORMATION.

Hollow celluloid articles are manufactured by three different processes, according to their nature, viz., stamping, moulding, and blowing.

By stamping are manufactured various boxes, needle-cases, brush handles, soap boxes, &c., balls and certain toys; by blowing are made dolls, animals, the handles of sticks, umbrellas, mattocks and children's carriages (all of which are made in a single piece), serviette rings and bicycle handles.

By moulding are manufactured certain toys, stick and umbrella handles in two pieces or massive.

The term moulding is generally confused with stamping, which consists in working a plate in a matrice with a stamp, while moulding proper is carried out in a mould composed of two parts giving the definite shape to the object.

The former operation will be denoted by its true designation of "stamping," while the term "moulding" will be reserved for the operation which consists in forming a celluloid object by compressing the material in the interior of a mould in two parts, whose hollows represent the projections of the piece to be obtained, with the introduction of a core into the interior when a hollow body is required.

We have remarked upon a tendency, most natural perhaps, of confusing under the same denomination of moulding the preceding operation of moulding proper and that which consists in applying the material to the walls of the mould by the pressure of steam injected into the interior of the material. This process is indeed a type of moulding but a special kind analogous to glass-blowing in a mould and to which the term of blowing is reserved.

Moulding consists, as we have seen in the comb manufacture for example, of giving the desired shape to a lump of material in the interior of a mould in two pieces under the combined influence of heat and pressure. We have described at sufficient length the moulding process for the comb, in order that stress need not be laid on the operation of moulding in general.

Stamping consists in taking a celluloid sheet and giving it a desired shape by hot pressing.

The use of heat is necessary in both kinds of operations, so as to impart sufficient plasticity to the material for avoiding rupture. This heating may be done in two ways, viz., by immersing the celluloid in hot water or by placing it upon heated plates. The moulds should be themselves heated by preference, in order to maintain the plasticity of the material for the necessary time during compression.

Whatever be the process employed the material should be very clean, and it is first necessary to remove from the surface all dust and foreign materials which may be deposited there, since these impurities, once introduced into the interior of the mass and distributed by compression, may no longer be expelled either by pumicing or polishing. For white articles especially, imitating ivory for example, this precaution is indispensable.

The material thus prepared is cut into sheets of shape appropriate for that we wish to obtain, either discs, rectangles or squares.

The softening is next brought about. For objects of small thickness, hot plates may conveniently be employed. When the objects are to be made from thick sheets it is preferable to have recourse to immersion in hot water, because softening is thereby brought about very uniformly and all danger of ignition is certainly removed.

In the latter case it is necessary to dry the celluloid sheet upon a hot plate before its introduction into the mould.

In the case of shallow objects the following process may be employed: the bottom of the mould or matrice presents in projection the hollow to be obtained on the object, *e.g.* covers, needle-cases, dishes, cups, boxes, &c. The celluloid sheet is placed between the two sections of a press-ring or frame, and the whole then placed in the press, the sheet having previously been softened. It thus rests upon the projecting base of the matrice, and by compression upon this base the sheet assumes the shape of the projecting part.

When deep objects are required, necessitating a very pronounced stamping, and thereby producing an appreciable drawing out of the material, the operation is performed under water, the material and mould being immersed at the same time in hot water during the whole duration of the pressing. Boxes, deep needle-cases, and accumulator baths are thus obtained in good condition. Articles of greater dimensions may also be made in a single operation on condition that the moulds are adapted to this kind of manufacture.

The operation requires great skill on the part of the operator. On the other hand also, the material should be of very good quality, neither too old, nor brittle, nor hard, since rents would be produced during the pressing, and the stamped or drawn object, to use an expression adopted by certain authors, would be easily broken in consequence.

In all these operations it is of advantage that the moulds should be perfectly polished, so that the object obtained does not require too prolonged and therefore expensive finishing operations.

In general, the angles should not be too acute, especially for deep objects, since the material may be much more easily worked when the angles are slightly rounded. Celluloid is not a malleable substance, and in consequence stamping out at angles which are too acute will risk breaking or seriously weakening the material.

In the case where sharp angled objects are required, it is preferable to

proceed in an entirely different way by forming the objects in several pieces and welding them together.

Finally, blowing is a process which tends to be developed. It has the advantage of economising much material, but against this a material of good quality is required. If the celluloid be not homogeneous the blowing will not be uniform, so that breaking or the formation of ridges and wrinkles will ensue; if foreign materials or cracks are present, it will break on blowing. The blowing may be performed on tubes or on two sheets joined together.

The tube will blow better than sheets, because it has not been compressed in the block, and the re-dressing and polishing presses, and therefore preserves greater plasticity. Also it returns much more easily to the pasty condition, and its walls will weld much better.

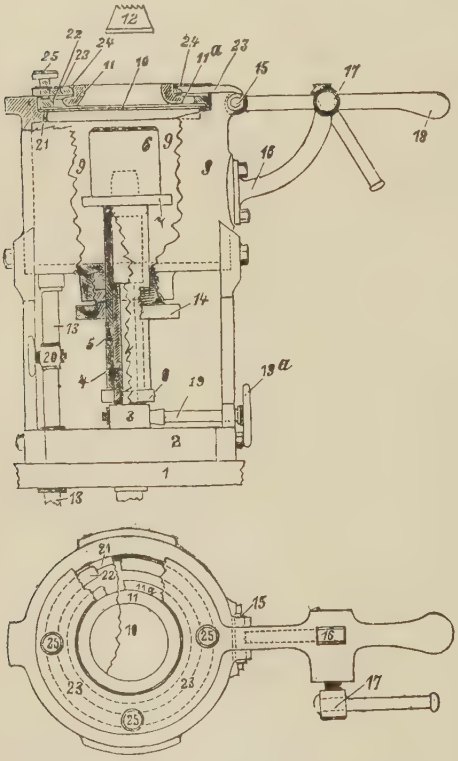


Fig. 123.

In principle, blowing consists in placing a tube or two sheets of material in a mould, and then injecting steam into the interior of this tube or between two sheets in order to apply them against the walls of the mould and so cause them to assume the desired form.

Ordinary steam, dry steam, or compressed air may be employed for the blowing process.

Such are the various methods employed for the manufacture of hollow bodies, the detail of which may vary from one firm to another and according to the articles made.

R. Stubling's Press for Stamping Celluloid Sheets. This press permits of manufacturing hollow bodies from a celluloid plate by the action of a simple punch without recourse to welding or to moulds. Any hollow shape whatever may be produced by the action of a stamp-carrying plunger upon a plate softened by steam, *e.g.* boxes, needle-cases, &c.

The softening of the plate is brought about by the steam from a small boiler acting upon the plates and also upon the stamp (Fig. 123). The apparatus consists of a work-table 1, bearing a plate 2, upon which rests a two-way valve 3, worked by a rod *cq*, and a wheel 1*qa*. Above this valve is a fixed hollow

plunger 4, upon which may be displaced the steam cylinder 5, which traverses, through a stuffing-box 14, the base of a small steam boiler 9. The upper part of this cylinder carries a plate 7, upon which the stamp 6 is arranged, fixed upon a cylindrical spindle. This stamp works upon the celluloid sheet placed at the side 21 of the boiler.

By means of a tension collar 22, the celluloid sheet may be tightened by a screw 25. The press collar 11, forming a matrice, is maintained in the cover by a rim 11*a*.

Steam is conveyed from the boiler 9 by the pipe 13, furnished with a valve 20. The lid of this boiler 22 is jointed at 15, and moved by a pinion 16, which is worked by a screw 17, and which acts upon the handle 18 drawing out the cover. The closing may be rendered air-tight from the side opposite by the screw 25, so that the handle 18 only serves for opening and shutting.

Between the cover and the ring 11, an asbestos ring is placed to avoid cooling. The boiler and steam cylinder carry taps for the withdrawal of the condensed water.

The apparatus works as follows:

By means of the screw 17 and the handle 18 the cover 23 is opened. The celluloid sheet is put into position so as to rest upon the seat 21, the ring 22 is placed and then the ring 11. The cover is closed and the screw 17 tightened. By opening the valve 20 steam issues from the boiler, and is sent into the punch 6 by the tap 3. Pressure is communicated to the cylinder 5 by means of water.

When the stamp 6 passes the collar 11 a current of water is sent which cools the celluloid so that it hardens, while that remaining in the heater is still in a sufficiently plastic state to be run between the pressure collar 11 and the stamp, the celluloid mass thus taking the desired form.

BALLOONS AND BALLS.

Balls are manufactured in two pieces formed into hemispheres and afterwards welded.

The hemispheres are formed by stamping out from two celluloid sheets.

Discs are cut by the punch from celluloid sheets, which are known by the trade term of "flons." Two of these flons are placed in a mould and lightly secured by a ring. The mould containing the flons is afterwards plunged into boiling water to soften the celluloid.

The whole is then placed under a lever stamping press. That part of the mould carrying the flons constitute the matrice, the stamp being carried by the movable part of the press. By acting on the press lever the punch is lowered into the matrice, and thus the shape of the mould is given to the celluloid. When the punch has arrived at the bottom, a sharp cut of the press detaches the part fastened between the ring which has not to be moulded. The mould is then placed in cold water to harden the celluloid, and thus

two moulded hemispheres are obtained, one in the other, which are separated. To form the ball these hemispheres are fitted to one another at their edges and welded with acetone. (Fig. 124*a*.)

For strengthening these balls, whose two halves are readily separated, the joint is sometimes furnished with a strengthening strip. Other arrangements

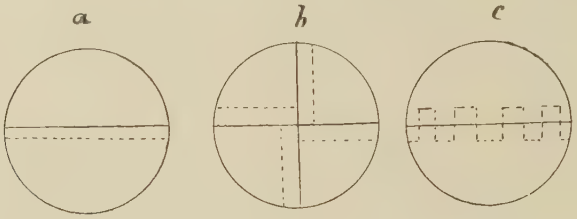


Fig. 124. Balls.

have also been adopted, consisting in dividing the ball into four sectors, which are reunited by strips. (Fig. 124*b*.) Nevertheless, these joints are uncertain and present the additional inconvenience of a large number of weldings.

Resort has therefore been made to other processes.

According to Böckmann the following may be used: each hemisphere is furnished with teeth, which are slightly inclined towards the inside of the ball,

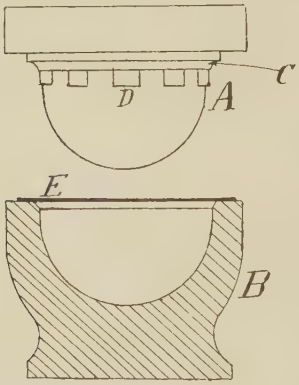


Fig. 125. A Ball Mould.

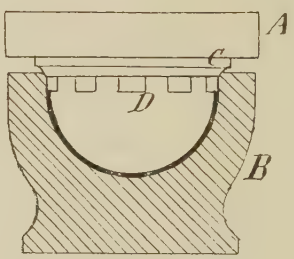


Fig. 126. A Ball Mould.

and the two halves are fixed so that the teeth of one are inserted between the teeth of the other, as indicated in Figure 124*c*. By fitting, the alternate teeth of each hemisphere come to be inclined towards the interior of the other hemisphere and the whole is then welded.

This process requires a special mould. The matrice is formed of one hemisphere, while the stamp is formed of another which exactly fits into the first.

At the upper part, however, the stamp carries a ring *C*, whose lower edge possesses upon its circumference the slightly conical teeth *D* so as to facilitate penetration into the matrice. (Fig. 125.)

The celluloid sheet *E* being hot pressed, the punch teeth drive back the material which remains in the intervals of the teeth *D*. (Fig. 126.)

The resulting hemispheres have their teeth slightly inclined towards the interior, and these are welded with acetone. The two hemispheres are fixed at the base and the teeth welded.

The following process, due to the Rheinische Gummi und Celluloïd Fabrik of Neckarau (Mannhein), uses a special spring press in three sections (Fig. 127) for the manufacture of the hemispheres.

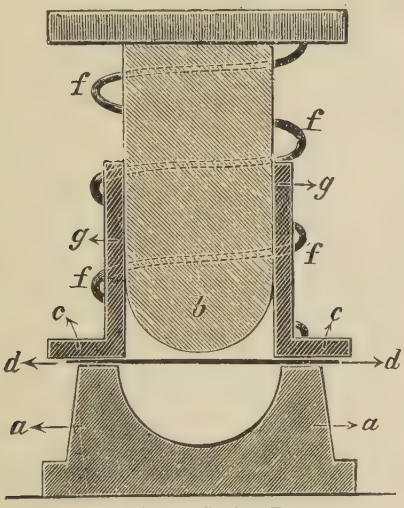


FIG. 127. A Spring Press.

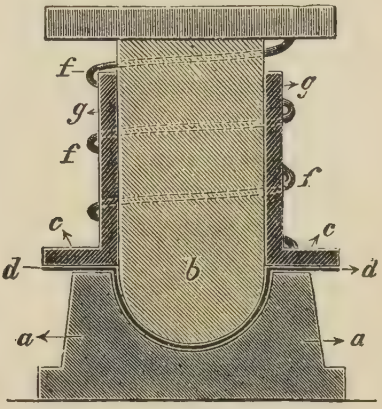


FIG. 128.

The bed *a* forms the matrice which is fixed; the upper part *b* is the stamp, and between the two a cylindrical collar *c* is inserted which maintains the sheet in position. A spring *f* presses the piston into the matrice forming the hemisphere, as indicated in Fig. 128.

Both hemispheres are then welded with internal reinforcement (Fig. 129A).

For greater durability the two hemispheres may be welded upon two others, whose seam is contrary to that of the external hemispheres (Fig. 129B); there is evidently a greater expenditure of material but the strength is more substantial.

This press has the inconvenience of only permitting the manufacture of a single kind of article, so that at present presses are used, for preference, which may serve for making objects of various shapes by inserting between the plates a mould in two parts, viz. a die and a stamp.

The lower part is formed of a block *B* pierced by a cylindrical cavity traversing it throughout and independent of the object to be manufactured (Fig. 130).

The stamp *A* (Fig. 130) is formed of a plate and a projecting part having the shape of the object to be made.

The block *B* has two lateral grooves, in which may slide two plates *C* and *D*;

these may be heated and possess an aperture corresponding to that of the block. The celluloid sheet *E* is placed between the two plates, and is thus at the same time maintained hot and tight. The sheet, previously softened and maintained

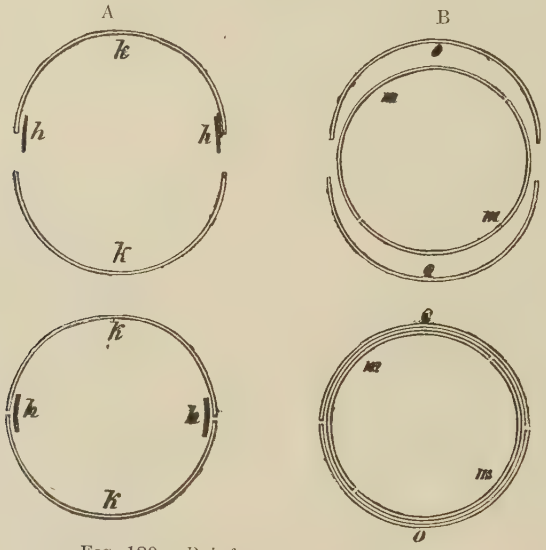


FIG. 129. Reinforcement of the Balls.

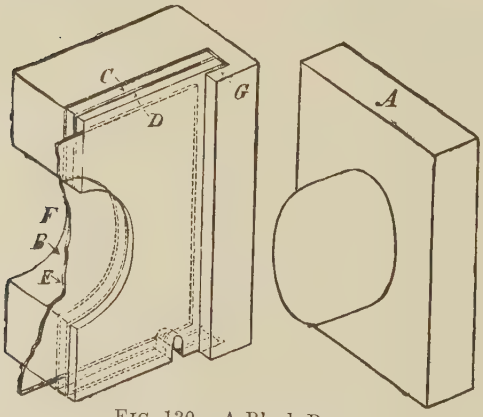


FIG. 130. A Block Press.

in this state, is compressed in its open part by the punch *A* under the influence of the press in which the whole has been placed.

The mould is then removed, the celluloid sheet replaced by another and the process repeated.

The operation may be very rapid, should the plates have been sufficiently heated so that the celluloid does not cool, but so arranged on the other hand that the latter is cool when the punch arrives at the end of its stroke.

The most certain process is still that pointed out at the beginning, and in which a mould is used instead of the block *B*. It may be applied for all kinds of objects by replacing the mould.

Moulding from a cast. As regards the seam, the process giving the best result from the standpoint of durability is that employed specially for balls imitating oranges, apples, &c., and objects imitating fruits, *e.g.* pears, &c. This is the process known as "moulding from a cast" (*surmoulage*), which permits of internal welding.

Balls, moulded or welded, are placed in a special hermetically closed mould. This mould is immersed in boiling water, so that the air contained in the interior of the ball may be heated, expand, and compress the object against the mould. The whole is then immersed in cold water, so as to chill the celluloid. A ball is thus obtained whose welding is almost invisible externally and which is very strong. By elaborating the mould the celluloid surface may be made to imitate oranges, apples, and various fruits.

CASES, COVERS, &c.

Boxes, cases, &c., are made by stamping in warm water, as for balls, by means of dies and punches having the requisite form.

For shallow boxes of small dimensions and thickness, hand moulding may even be performed with pincers. The pincers comprise at one extremity a small die, and at the end of the other branch a stamp fitting into the die, with the necessary play for a definite thickness of celluloid. The celluloid disc is placed between the two extremities of the pincer, whose arms are long enough to afford a leverage for exercising sufficient pressure. The sheet is tightened by squeezing gently the pincer arms, and the whole immersed in hot water, where the celluloid softens, and is then compressed strongly by hand.

For objects of much larger and deeper dimensions, it is necessary to employ a stamp and die, and to operate with a screw, fly or knee press, or a small hydraulic press.

For very deep boxes, such as powder-puff boxes, it is necessary to resort to drawing with a special press, whose lower portion and the whole of the matrice are immersed in hot water. The drawing is then carried out slowly and progressively to great depths, without any fear of the material breaking as in the case of ordinary presses.

It is unnecessary in this case to use the fly press, which is too rough, works rapidly, and by drawing out the material abruptly produces cracks and even rents. The lever or screw presses are preferable.

When the object is drawn out, the mould is withdrawn and chilled in cold water. This excellent process, requires nevertheless much experience on the part of the workman, especially for gauging the necessary period of immersion. It necessitates also a very good material, as we have seen.

Boxes with sharp angles are made in two sections, the one bent and welded

with acetone forming the body of the box, the other stamped out with a slight rim is welded to the body forming the base. It is thus that accumulator boxes with sharp angles are made, but they are also manufactured by drawing out in the case where the angles may be rounded off.

DOLLS, ANIMALS, RATTLES.

Formerly dolls, animals, fruits, rattles, &c., were made by the moulding process; at present blowing is preferred.

The manufacture is well developed in Germany, but up to a little while ago was still unknown in France. Now these objects are manufactured at Chauffry by the Société Industrielle de Celluloïd, at Etain by the Etablissements Petitcollin and at Oyonnax by the Société Convert.

Either the tube or two celluloid sheets joined together are employed. The former process was patented by the firms Reich Goldmann und Scheiner of Offenbach for the manufacture of dolls, religious images and furniture (*nippes*), the latter was patented by the Rheinische Gummi und Celluloïd Fabrik of Neckarau (Mannheim) for the manufacture of dolls.

The oldest process, and the least in use at present, consists in passing steam under pressure through a celluloid tube placed in a mould without preliminary heating.

The steam under pressure applies the tube as it softens to the walls of the mould. The current of steam is then replaced by one of cold water at the same pressure, so as to avoid contraction and deformation of the moulding. The mould is released and removed. The tube is then closed at its extremities by welding.

This process is employed for stick and umbrella handles, serviette rings, &c., in which it is only necessary to enlarge the tube. It possesses the drawback that the steam, containing water, moistens the celluloid.

Blowing by dry steam. The process comprises the same operations as the preceding, only the steam is previously passed through a water separator, which removes the water carried along. The celluloid is softened but not moistened, and not being deteriorated, endures much better the welding operations necessary for afterwards closing it at its ends.

The tube may be replaced by two celluloid plates.

Blowing by compressed air. Finally steam, even when dry, has been replaced by compressed air. The mould should then be heated and cooled externally, either by a passage of steam into the body of the mould or by heating the press. There exists therefore no contact between celluloid and water, either on heating or cooling, and a much better welding is produced.

For this process ordinary presses may be employed, but hydraulic presses are much more economical. M. Bouchholtz of Paris practises the process in the following very economical manner: The blowing is done by compressed air in the hydraulic press. In a corner of the works is the accumulator for starting

the presses. The latter are grouped in fours around an iron table heated by steam circulation. The steam and cold water pipes pass underground. The installation of these four presses and the table occupies 6 by 12 square metres, according to the power. The hydraulic plant occupies about 10 square metres.

The operations are as follows:

Upon the table, heated to a constant temperature, are placed the mould and the two celluloid sheets. When the latter are sufficiently softened they are placed between the two halves of the mould, which is then placed under the press and the low pressure turned on. The hot air inlet is then opened for about a minute, and the high pressure turned on for a few seconds. The object of the low pressure is to close the mould hermetically while the high pressure welds the two plates to each other. The compressed air applies the celluloid against the walls of the mould.

When the operation is over the mould is cooled under pressure by a continuous circulation of cold water.

As in all moulding operations, the pieces emerge encircled by a thin coating of celluloid. This coating is cut, and at the same time the different pieces obtained side by side in a single operation are separated, and the weldings pumiced.

The celluloid employed should be of very good quality, and its thickness ordinarily vary between $\frac{3}{10}$ and $\frac{6}{10}$ of a millimetre. It is necessary to exercise care when closing the mould to ensure that the whole of the celluloid mass is suitably and uniformly softened. The setting of the mould, and subsequent closing, should be executed rapidly to avoid a cooling of the mass.

If the objects are to be coloured, the tints, either in light and shade or uniform, may be made as desired by means of a colour vaporiser. This process is rapid and economical. The same workman superintends four presses at once so as to avoid loss of time, and the average duration of a complete operation is about 12 minutes for the simultaneous blowing of the four moulds.

It will thus be seen that a real economy in time and manual labour is effected by the above process. A very good material and a carefully constructed plant are alone demanded in order to avoid miscalculation.

Dolls, animals, rattles, &c., are thus obtained.

Concerning dolls we shall only mention here the process for manufacturing joints by Buschow and Beck (Andès, Celluloïd und Seine Verarbeitung) for dolls in several jointed pieces. We shall describe the coloration of objects according to Krammer and Reinhardt's process (Walterhausen, in the chapter "Decoration of Celluloid").

ACCUMULATOR BOXES.

Celluloid is naturally employed for accumulator boxes. It is not attacked by acids and is a sufficient insulator. It has also the advantage of lightness, which is most valuable for accumulators.

Accumulator boxes of sufficiently large dimensions are placed in the category of hollow articles formed in sections and welded by acetone. The body is constituted of a sheet bent at sharp angles and welded. The bottom and lid are welded to it. The bottom should be strong enough to resist deformation. The cover, however, demands most attention. It should be perforated by several apertures: two for the passage of the terminals, a larger one for filling the accumulator, and a smaller for the gas to escape. The latter is necessary for avoiding deformation and warping, which are frequent in closed accumulator boxes where this precaution has not been observed.

These orifices are ordinarily furnished with small tubes or collars formed of a circular plate, surmounted by a small cylindrical collar, the two pieces being welded by acetone on account of the sharp angle formed between them. The firm of Hemmen, at Lilas near Paris, makes them, however, in a single piece, which increases their strength.

Accumulator baths are also made without lid, and may be obtained in sections, if they are of large dimensions with sharp angles, or in a single piece in the contrary case.

SPECIAL PROCESSES FOR MANUFACTURING HOLLOW BODIES.

Process of the Offenbach Celluloid and Caoutchouc Works of Kohl & Wegewroth. The object of this process is to obtain hollow articles by the progressive action of compression and heat upon a celluloid sheet. The sheet is pierced and curved by stamping; then the celluloid is driven as far as the bottom of the matrice, but is curved and brought into shape before the celluloid can move away (German Patent 177622).

By this process, for example, are manufactured thumb-stalls and rings. The mould is composed of three sections (Fig. 131): the basal plate *a*, the covering plate *c* forming a punch, and the intermediate plate perforated with apertures forming the matrice.

In order to manufacture thumb-stalls, for example, a sheet of celluloid *d* is arranged upon the matrice *b*. By stamping with the plate *c* the sheet is pierced and the celluloid driven into the hollows of the matrice, so as to give it a shape similar to that of the mould (Fig. 131B). Then by pressure an elongation of this shape is brought about and the celluloid pressed so as to obtain the definite shape required (Fig. 131C).

The first phase of the compression forms short conical tubes in the sheet possessing collars *d* (Fig. 131B). If the pressure be continued these tubes are enlarged at the same time as the walls are thinned, the celluloid passing towards the lower part of the matrice.

The plates are such that when the angle *g* of the upper plate just touches that of the intermediate matrice, *i.e.* presses upon the collars, only the base of the matrice remains to be filled, and the celluloid constituting the collars is sufficient with a little pressure to fill the space destined for the base. From

this point the compression removes the collars (Fig. 131c) and drives the celluloid into the basal space. The lower plate *a* is for this purpose engraved into hollows for forming this base.

Objects are thus obtained fairly homogeneous and compact with the thickness of a sheet of paper.

This process may be compared in principle with that employed by the Rheinische Gummi und Celluloïd Fabrik for moulding combs. While the object may be produced entirely by chasing out (in the comb by stamping out), which if deep enough would tear the material, at the same time the compressed celluloid is forced to fill up the spaces.

If rings are to be manufactured (Fig. 132), suitable moulds in three pieces are arranged (Fig. 132), and the operation is the same as above. The celluloid sheet is first chased out by the punch of the upper plate; then, as this punch continues its descent, the material is compressed no longer into the cylinder *p* but into the ring *q* on each side, as indicated in Fig. 132c. Finally, the punch meets the base of the cylinder *p*, the celluloid has been driven entirely into the ring, and is there under slight compression. Channels *r* are provided for the escape of the air compressed by the punch. Finally it is necessary to be able to withdraw the moulded piece, which behaves as a core. For this purpose the matrice *b* is in two sections (Fig. 132E), which are firmly secured by pins or tightened by pressure.

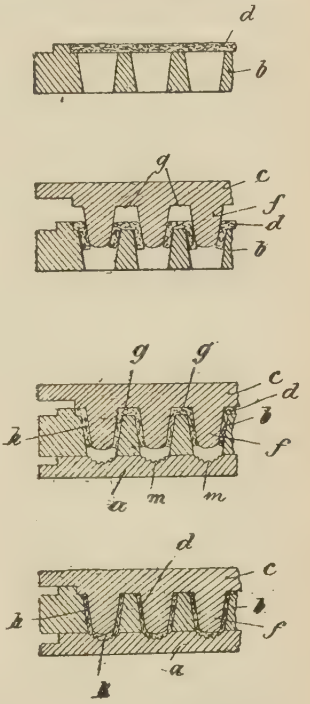


FIG. 131. Process of the Offenbach Celluloid and Caoutchouc Works.

CAPSULES AND RING STOPPERS.

Capsules and rings for closing vessels are made of celluloid by combined pressure and heat, as in the case of ordinary hollow bodies, followed by cooling. They are next fixed upon the recipients by compression upon the neck. That property of compressed celluloid is here utilised of taking up again its original shape when heated. As a preliminary it is brought to a narrow and expansible shape, which expands to form the capsule when heated; it is allowed to cool while prevented from contracting, and an enlarged shape is thus obtained. On heating again the capsule resumes its shape. The following method is employed for fastening capsules upon the neck of the receiver so as to obtain hermetic closing. The capsule is placed on the neck, and the whole immersed in hot

water. The capsule readily tightens under the influence of steam and closes upon the neck. Pressure may also be employed by any process whatever.

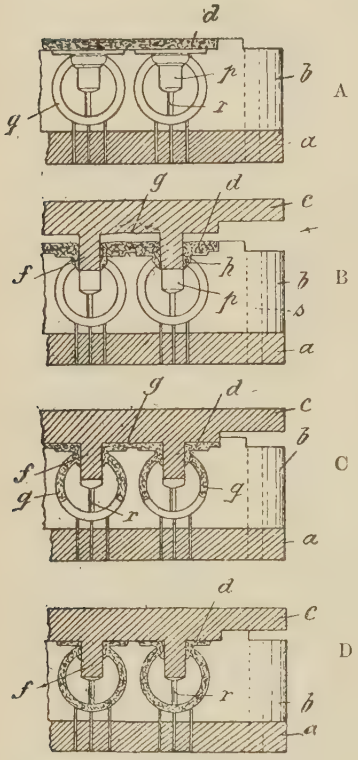


FIG. 132. The Offenbach Process (rings).

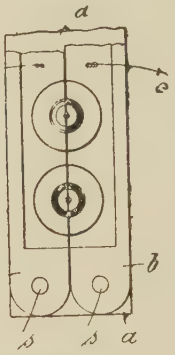


FIG. 132.

FIG. 133.

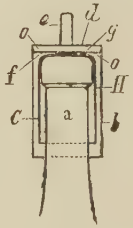


FIG. 134. Engels' Process

Ewald Engels' process. The following process has been patented by M. Ewald Engels (German Patent 171704).

It consists in violently compressing the celluloid capsules or rings heated with steam (*see* celludin). It is practised in the following way:

The celluloid, previously shaped by a cylindrical die, is placed upon the neck of the vessel to be covered, *e.g.* a bottle. It is covered by a metallic cap having single or double walls. In the former case the cap is constituted of a tube *b* forming a case and a cover *d* traversed by a steam inlet tube *e* (Fig. 134). The celluloid *C* is placed in this cap *H* upon the upper part *a* of the vessel. An intermediate wall *f* separates the cover *d* from the cap cavity, and a hole *o* perforated in this intermediate wall permits the entrance of steam between the inner face of the cap wall and the outer face of the celluloid capsule. Steam is admitted into the cap and, at the same time as it softens the celluloid, the latter

is applied to the walls of the vessel and has the desired shape imparted to it, constituting a hermetic seal. The cap should be of sufficient weight to resist the force of the steam which tends to make it swell. The condensed water is withdrawn at the lower open part. In the case where the cap has a double wall, the inner chamber is furnished with a tap for the condensed water and the intermediate wall *f* may be abolished.

For rings a slightly different arrangement is used.

The cover *i* being placed on the vessel, the ring *r* fastens the cover upon the neck. The cap includes a mantle *b* and a pressure-piece *k*, provided with grooves *n*, which is applied to the bars *p* by the pressure of a spring *s* upon the pieces *m* (Fig. 135).

The cap *b* is furnished with a handle *l* for turning it. When by rotation of the cap through the handle *l* the grooves *n* are brought under the bars *p*, the spring *s* pulls the piece *k* upwards and liberates the cap which presses upon the ring.

To compress a ring by this process, the various parts are brought to occupy the position represented in Fig. 135 in which the pressure-piece *k* is raised with the cap *b*. The bars *p* prevent *k* from being raised, and cause it to rest upon the cover *i*.

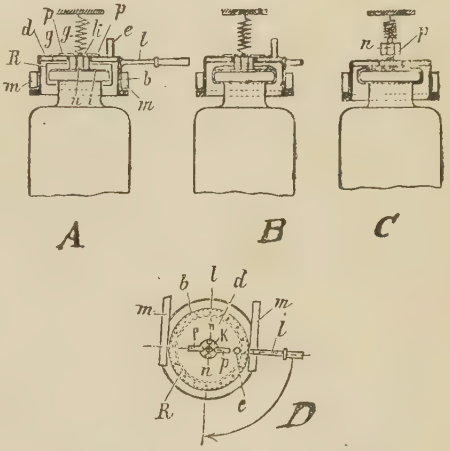


FIG. 135. Engels' Process (stoppers).

Steam is then admitted by the tube *e* into the chamber *g*. The ring *r* is compressed, deformed, and moulded upon the edges of the vessel's neck. The handle *l* is then turned so that the bars *p* work in the grooves of the piece *k*. The spring raises this piece, the cap is lowered and the ring compressed.

Screw closing capsules. By the general contraction process indicated above, screw stoppers may be produced. The capsules or covers are previously formed of narrow dimensions, which are afterwards enlarged as above. They are then placed upon the threaded neck and immersed in hot water.

WILHELM LUDOVICI'S PRESS.

This press is particularly employed in the case where the entire body of the press should be heated during the operation. In reality it permits of automatic heating and cooling without transporting the mould into a bath.

The press frame *A* (Fig. 136) is placed in a vat of hot water *k*. This frame carries on one side the press table *a*, and in another part the guide sliding block of the punch *b*. The table may be displaced by a spring *c*; the punch *b* may be displaced vertically by means of a lever *c*, movable about a pivot *m* carried by the

frame and controlled by a connecting-rod *n*. This connecting-rod is joined to a counterpoise lever *f* which is connected to the piston of a pump. It is the movement of this lever which causes the piston *g* to work in the barrel of the pump.

The pipe *i* connects the pump with the chamber *h* in which the pump is placed.

The press functions as follows:

The vat *r* is first filled with hot water to about 10 mm. below the matrix. A plate of celluloid is placed on this matrix, and the punch then set in motion

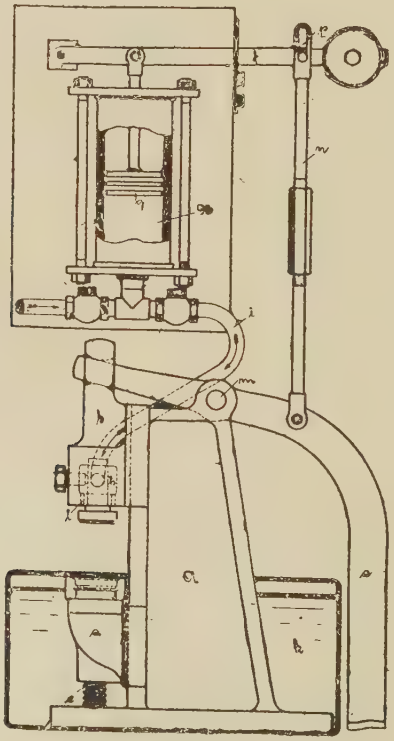


Fig. 136. Ludovici's Press.

by the lever *c*. The pressure commences by compressing the spring and lowering the matrix below the water-level. The celluloid plate is softened by the hot water. As soon as the spring will no longer be compressed pressure is exercised upon the celluloid and the stamping out takes place. When this operation has ended the lever *c* is lowered, this raises the punch, at the same time drawing back the lever *f* by the connecting-rods *n*. This lever works the pump piston, cold water flows through the pipe *i* into the punch chamber, and the cooling takes place. We have, therefore, an automatic heating and cooling.

CHAPTER V

CELLULOID LINEN

AMERICAN LINEN.

Linen constitutes with combs, umbrella handles, dolls, pearls, and films, one of the most important of the celluloid manufactures. Celluloid linen, also known as American linen, is well known and has achieved a very great success.

For this purpose a special celluloid is used which has received the name of supple celluloid. It is a celluloid rendered supple by the incorporation of castor-oil. Zinc white is also added so as to obtain a strong white appearance. White lead is avoided because of its turning yellow, which changes into grey after a certain interval.

The primary material is employed in the state of sheets of thicknesses varying from 12 to 50 hundreds of a millimetre according to the quality of the linen, *i.e.* the strongest is half a millimetre thick. These sheets are separated by cloths to avoid one adhering to another.

The manufacture comprises six operations after a preliminary testing of the primary material, viz., cutting, sizing, ironing, pressing, drying, pumicing and polishing, glossing, planing, pitting and button-holing.

The preliminary operations are the testing and cleaning of the primary material with the object of classifying the sheets according to thickness and putting aside those soiled by foreign materials.

The thickness is tested and the sheets classified in categories by $\frac{1}{100}$ ths of a millimetre, $\frac{12}{100}$ ths, $\frac{13}{100}$ ths, up to $\frac{50}{100}$ ths.

The soiled sheets are submitted to a cleaning operation which consists in eliminating by the scraper the foreign substances such as particles of iron, wood, straw, &c., proceeding from the storage and packing. The soiled parts are carefully and gently scraped with a fine well-sharpened blade.

CUTTING.

The cutting operation consists in cutting up the celluloid sheets according to the shape desired for the article to be obtained, and may be carried out by the ribbon saw or punch.

The latter is naturally more rapid and economical, but only allows pieces to be cut according to fixed sizes and shapes. A certain number of current sizes and shapes should therefore be chosen, so as to have a limited number of punches. Moreover, there is no greater inconvenience as regards sizes and shapes than in the manufacture of collars and cuffs.

For fancy shapes the ribbon saw is employed for preference, which permits

of cutting contingent designs. The punch is that usually employed in operations of this kind with current stamping presses, either plate or carriage.

M. Béthisy, in *Le Caoutchouc et la Gutta-Percha*, recommends the use of a cutting machine which offers, he says, the double advantage of allowing new designs to be made without great expense and avoiding the purchase of an expensive punch.

We believe that the expense occasioned by the purchase of the punch, and the inconvenience of arranging on the one hand the punch, and on the other the ribbon saw, are compensated by a much greater productive capacity of the punch than the cutting machine could attain.

The cutting is made upon a definite number of sheets. It should always be made at slightly greater dimensions than those required, because it is necessary to allow for a slight contraction. One proceeds by dividing the sizes into two, the equal sizes on the one hand and the unequal on the other. The equal sizes are cut first of all, then the whole of the unequal so as to avoid mistakes. The size is immediately marked on each parcel.

Cutting by the punch. Cutting is practised upon 10 to 12 sheets at a time, The sheets are placed upon the carriage and cover the punch. A press cover, usually of commercial celluloid of thickness from 10 to 12 millimetres, is placed upon this carriage and the carriage pushed towards the rear. This movement works the press plate, which descends, and applying the punches cuts the sheets. The object of these celluloid covers is to avoid the operating table of the carriage being injured by the cutting. After being cut by the punch, another movement places the sheets out of action, and others then take their place. The stroke of the plate should also be carefully regulated. In cases where this stroke is too short, it is obvious that the whole sheet depth will not be cut; where however the stroke is too long there is the risk of breaking the punch, while the celluloid covers, which have the effect of moderating the shock, may be exceeded.

For each piece, collar, cuff, &c., it is necessary to cut two sheets of different dimensions and one of cloth. The latter should have the same size as the smallest sheet, and is also cut by the punch. Two punches are therefore required for each size, one for the sheets having the shape of the collar or cuff and for the cloth, the other for the celluloid sheets which should project over the first.

Cutting with the saw. The cutting is made by means of an ordinary ribbon saw. As when punch cutting, 10 to 12 superposed sheets are cut in a single operation. These sheets are placed on the saw bench and fixed by means of clamps. Upon the pile of sheets a sheet of sufficiently thick foolscap is placed, upon which the contour of the object to be cut has been traced by means of a zinc pattern, and the cutting is made according to this contour. To avoid heating the celluloid, which would take place without fail under the influence of the saw and constitute a danger while deteriorating the material, sheets of ordinary foolscap are inserted between the celluloid sheets.

The cloths to be placed between the celluloid sheets are cut in the same way, but the saw blade employed for this operation is a little different, being without teeth and known as "*lame à couteaux.*"

As soon as the cutting is at an end, the pieces are classified according to size in bundles of a dozen, upon which the size is indicated. The pieces should be tested after cutting. Usually a girl is in charge of this operation, and tests the pieces, classifying them according to size and species, afterwards distributing them to the pasting room.

PASTING.

Pasting consists in welding to one another in the following order: (1) the large celluloid sheet; (2) the cloth; (3) the celluloid sheet of correct dimensions.

The operation is performed in the following way upon a table known as the pasting table, formed by a long table whose centre is occupied throughout the length by a shelf upon which the finished pieces are placed. On each side of the table, and facing each other, are the operators, who are usually women.

The pasting comprises four phases: steeping the cloth, draining the cloth, superposition, and compression or welding.

Steeping consists in soaking the cloths in alcohol to make the celluloid adhere. The cloths when cut are soaked by immersion in alcohol.

Draining consists in removing the excess alcohol by squeezing the cloths between cloth towels and zinc plates under a press, and recovering the alcohol in baths.

The superposition of the pieces is made by women, to whom the drained cloths are distributed in dozens. The woman first places a thick zinc sheet upon the table, covers it with cloth, then places upon it the larger celluloid sheet, next the cloth sheet, which is so arranged that there is a uniform celluloid border all round, and finally the second celluloid sheet. The whole is covered by a second thick plate of zinc, itself wrapped in cloth.

The pile is then carried in bundles of ten to twelve to the welding operation. This is performed by compression in a plate press, either in the cold or under the influence of a mild temperature given by the circulation of steam through the plates. Hot compression is preferable. This operation lasts from five to six minutes, and at the end of this time the welding is complete, the pieces are removed and conveyed to the ironing-room.

IRONING.

This operation consists in causing the projecting part of the larger sheet to form a hem over the narrower sheet. It is performed by box irons analogous to those used by tailors, or with ordinary irons. The celluloid softened by the hot iron is easily ironed out; the piece is then glided under an iron plate furnished with a cloth cover to avoid soiling the collar. It cools under this plate, and may

next be delivered to the receiver. Like the welding operation, it is performed upon a large table whose centre is occupied by a series of steam-heated plates, upon which the irons are placed. The ironing is done by women, who stand at each side of the table facing each other.

The finished pieces are tested by the receiver, who classifies them according to the way bill made out at the beginning of the manufacture, and accompanying the pieces through all the phases of their manufacture.

COMPRESSION OR PRESSING.

The hems formed by ironing are not welded to the pieces, so that this operation is necessary. It is carried out by submitting the pieces to compression or pressing.

This operation is made by means of lever presses, or, better, by hydraulic presses with steam heated plates. The pieces are arranged by operators known as "*plaqueuses*" upon a table situated behind the press. These workers first place a plate of zinc, a sheet of caoutchouc, and a thin cloth or press towel, then the piece to be pressed, above which in reverse order are placed a thin cloth, a caoutchouc sheet, and a zinc plate. The object of the cloths is to impart the twill of the cloth to the celluloid pieces, giving the appearance of linen.

The operator ("*enfourneur*," a putter-in) stationed behind the press superposes a certain number of these plates and places them between the press plates. At the front of the press stands the presser and the takers-out (*défourneurs*). The celluloid is rubbed with talc to avoid the towels being welded to it.

This operation demands a certain skill on the part of the operators. A suitable temperature must be obtained and not exceeded. The current temperature is from 60° to 70°, and it is unnecessary to go beyond the latter. The pressure is from 40 to 50 kilogrammes per square centimetre, and the duration of compression from three to ten minutes.

DRYING.

The welded pieces are subjected to drying in steam-heated chambers, whose rails are formed of iron upright and cross-pieces, and the cases of stiff cloth. The duration of drying is from eight to ten days.

PUMICING AND POLISHING.

The celluloid linen should be subjected, like other articles of the same material, to polishing.

This operation is carried out by pumicing and polishing rollers, analogous to those employed in the comb manufacture. A cylinder made up of discs of unbleached canvas for pumicing, and woollen cloth for polishing, is mounted upon a shaft. The discs are about 20 centimetres in diameter, and 5 to 6 in thickness. Between each of these is inserted a quarter or a half disc, the object

of which is to avoid heating. The rollers revolve at great speed, so that, in spite of the spaces formed by these semi-discs, the rigidity promoted by the centrifugal force is perfect.

These rollers are fixed to two puppets or supports by wooden plugs. A wooden trough filled with powdered pumice called "*ponce soie*," moistened with water for pumicing or with tellurine (levigated chalk) for polishing, is placed under the rollers.

The pieces for pumicing are placed upon boards covered with glass plates, and successively presented to the pumicing roller, which first of all removes the talc coating, then smooths and imparts to the pieces a dull uniform appearance. The polishing, which gives a beautiful gloss, is only practised upon pieces destined for the well-known glazed linen (*linge glacé*). The pieces are next washed with a large volume of water to rid them of the pumice sediment, drained, wiped, and dried.

Pumicing and polishing are also naturally made by machinery similar to that for combs.

The polished linen passes to the finishing department, there to be subjected to the operations of smoothing out, beating out, pitting, and button-holing.

SMOOTHING OUT.

The pieces, during the different operations and when drying, assume a warped and curved form. In order to straighten them they are submitted to a smoothing-out operation, which consists in heating them and smoothing out by hand upon steam-heated plates, afterwards chilling by means of a circulation of cold water through the plates.

BEATING OUT.

This process is applied to collars. The operation is made upon spheres or cylinders rounded at the top and placed vertically upon a table. The collars are beaten upon a hot sphere and chilled upon a cold one. This operation demands great skill and is very laborious. The workmen protect their fingers with finger stalls, and have to exercise great skill in beating uniformly.

PITTING.

Hem-stitching is imitated by rolling rowels, mounted with spurs, over the piece to the distance desired.

The operation is made by mounting the pieces upon a carrying cylinder driven by a pulley. The piece revolves upon the cylinder between two guides adjusted to the desired distance, and able to follow the contours of the hem. A rowel, worked by a pedal, traces at the same time a pitting upon the piece. This operation demands great experience ; a good operator may pit up to 100 dozen per day. At the present day the imitation of stitching is most

usually carried out by a passage between two roller cylinders which carry projecting points for pitting, these forming hollows upon the objects.

BUTTON-HOLES.

Button-holes are cut by the eccentric press. The upper press plate carries two punches, which form the outer button-holes. The pieces are slightly bent for introduction under the punches, by pushing them under guides which maintain them in position.

The centre button-hole is made by a press having a single punch. The two outer button-holes are placed in the bars of a parallelogram which are relaxed by pressing the piece under the punch. The button-hole is thus perfectly

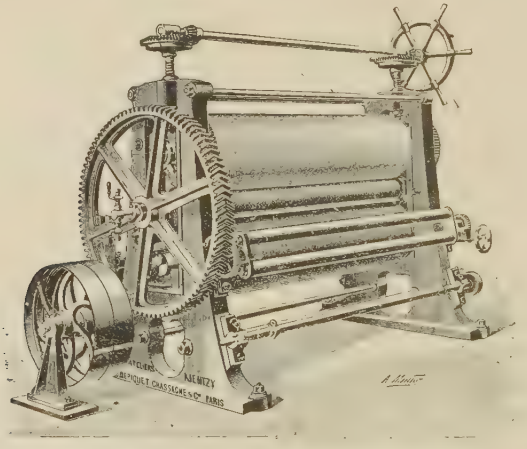


Fig. 137. Repiquet-Chassagne's Goffering Machine.

centred. This work should be carefully tested. The button-holes are also made by stamping at the same time as cutting.

The firm of Lend, Bensinger and Co., of Neckarau, near Mannheim, have patented a process for strengthening button-holes, which constitute the weak part of celluloid collars and cuffs. This process consists in inserting a tissue between the two celluloid sheets. By hot stamping the collar and button-hole are formed at the same time.

To-day the operation destined for giving cloth texture to celluloid, by inserting cloths between the celluloid sheets during pressing, has generally been suppressed, and this texture imparted by the same operation as that for imitating machine stitching; also two different machines may be employed, although both operations are made mechanically. The texture is given by the goffering machine. This machine comprises two heated cylinders upon which is a fine engraving imitating cloth. The collar, cuff, &c., is passed between the

two cylinders, and the hot pressure imprints the engraving or texture upon it. (Fig. 137.)

The finished pieces are packed, *i.e.* gathered in dozens of similar pieces, packed and classified in boxes according to size.

The manufacture of American linen has been widely extended. According to M. Béthisy (*Le Caoutchouc et la Gutta-Percha*, 1910), 400 to 500 dozens of collars, cuffs, cravats, &c., are manufactured in Europe per day, representing 2000 to 2500 kilogrammes of celluloid. It is largely manufactured in Germany, but the French manufacturer appears more appreciated. La Société de Chromolithie, at Paris, has acquired a justifiably high reputation.

CHAPTER VI

PRINTERS' BLOCKS. STAMPS. ARTIFICIAL TEETH. PHOTOGRAPHIC CYLINDERS

PRINTERS' BLOCKS.

Celluloid permits of obtaining good stereotyped plates, which possess certain advantages over wooden blocks. The substance penetrates especially well into the hollows, reproducing them with a delicacy greater than that obtained in electro-plates. In order to obtain a stereotype, the wooden block is first covered by a cement moulding, which advantageously replaces gutta-percha, since it hardens and may be removed without damaging the engraving. On the dried moulding thus obtained a celluloid sheet, previously softened by heat, is superposed. The whole is then placed under a press for five to six minutes. The complete operation requires about half an hour, and a reproduction is obtained superior in certain respects to those obtained by electro methods. Nevertheless, the use of these plates has not been general; the cause will readily be seen in the danger of conflagration entailed by storage, and perhaps even more by the administrative formalities which the storage involves.

The cement moulding in this operation plays the part of matrix. On account of the plasticity of celluloid, it has been proposed to utilise this for producing the matrix itself. It is then necessary to employ for the matrix a celluloid having a less tendency to be softened by heat than that of the plate to be obtained, so that during compression the matrix may not be softened or adhere to the softer celluloid plate. This result may be obtained by adding some zinc white to the celluloid destined for the matrix, while oil is added to that for the plate.

Better results are obtained by replacing celluloid with hardened caoutchouc.

According to the patent of the Société Anonyme Petitcollin (French Patent 387838), the celluloid matrix is replaced by a metallic one. This patent contains an interesting application of celluloid blocks for the reproduction of embroidered lace and ornamental textures, either in hollow or relief. A block of heated celluloid is placed on the press plate and covered by the lace work. Upon the latter a smooth steel sheet is placed and submitted to pressure. This causes the lacework or embroidery to penetrate into the celluloid, and form an impression in hollow upon it. A plate is then made by any ordinary process and the design can be reprodnced in its actual size in the catalogue.

Stereotypes may also be obtained by photography in the following way: a photographic proof of the design to be reproduced is taken and a negative made. This negative is transferred to a celluloid sheet covered with an albumen film. In order to obtain a stereotype with this photograph the above sheet is treated with a solvent: ether, alcohol, amyl acetate, or better with a mixture of these solvents, which attacks the celluloid in the parts not affected by sunlight and laid bare by development, but leaves intact the albumen film. The stereotype may then be used for making impressions upon paper. As solvent, for example, a mixture of 75 per cent. amyl acetate with 25 per cent. amyl alcohol may be used, and the proportion of amyl alcohol increased according to the depth of attack desired.

Gustav Zeidler proposes the following process for obtaining both a negative and positive together, *i.e.* a hollow cast and one in relief. For this the stereotype to be reproduced is placed upon a celluloid sheet, softened by heat and compressed. On cooling, a stereotype is obtained which is placed upon another heated celluloid sheet, and the two compressed together. Two reverse plates are thus obtained and either utilised according to requirements.

Although these different processes may yield the satisfactory results attributed to them by their authors, yet the use of celluloid plates has not been general.

STAMPS.

Celluloid stamps possess great elasticity, wear away much less rapidly than caoutchouc, and permit any kind of ink to be employed, which is a decided advantage.

Their manufacture is similar to that of stereotyped plates. They may be produced by means of metallic models, carrying in projection the hollows to be obtained upon the stamps, but this method is expensive and plaster moulding is rather employed.

The model, writing, image or ornament is placed upon hard wood or stone, and the stereotyped plate surrounded by a metallic frame of dimensions a little smaller so that the sides may be well supported. The inner sides of the frame are oblique, which allows the plaster to be easily removed. In these sides are two small interior grooves, into which the prongs of a small fork may penetrate for withdrawal of the mould.

This mould is made of plaster, modelled very delicately and recently, because if old it would not cohere.

For easy removal, the stereotype is oiled by means of a soft brush of about two centimetres diameter, employing a hot mixture of 32 parts spirits of turpentine, one part olive oil, and one part of white copal. The plaster is mixed so as to be fairly liquid, then poured upon the entire surface of the stereotype, being made to penetrate its hollows by a hard brush, the upper part being then removed. The plaster hardens, and after five to six minutes it

may be detached by slightly tapping the frame and using the small fork introduced into the grooves.

Matrices are thus obtained which may be dried upon 12 to 15 pieces of wire gauze distant about 2·5 centimetres, and forming the shelves of a stove heated chest. The drying lasts about two hours; it is considered at an end when the moulding takes a slight yellow tint and appears brittle when struck. This drying is very important, because any trace of moisture in the mould involves its rupture under pressure, or gives defective celluloid plates. It is next coated with a little gum-lac solution to polish the surface and add to its permanence.

In order to manufacture a stamp with this material the method is similar to that for stereotypes, by placing above a celluloid plate softened by a heating with warm water at about 70° C. Both are then subjected to pressure for five minutes in a press, whose plates may be steam heated or chilled by a cold water circulation. The cooled stereotype is then removed.

ARTIFICIAL TEETH.

Celluloid presents over caoutchouc, when used for gum plates, the advantage of not being coloured red by cinnabar, since this colour comes off and has already produced mercury diseases: *e.g.* diarrhœa, inflammation of the gums &c. The colour of caoutchouc is superficial while that of celluloid, like cinnabar, is throughout the mass. Celluloid imitates the gums much better than caoutchouc, and is worked up more easily.

To make artificial gum plates, a plaster mould is first made as in the case of stereotypes, stamps, and ink rollers.

This mould is obtained by taking an impression of the jaw with slightly softened wax, which is then allowed to harden. This imprint is covered with plaster in a basin, and heated after the plaster has hardened, so as to dry the mould and cause the wax to melt. It only remains to mould a celluloid sheet by heat and pressure upon this matrix. The operation differs somewhat from the moulding of stereotypes and stamps.

The forms of apparatus employed for this moulding are all derived from Jüterbogk's apparatus, and present many analogies with those serving for the manufacture of vulcanised caoutchouc gum plates. They comprise a case and a basin enclosed in a boiler and compressed by a screw passing into a stirrup, arranged so that the screw pressure acts upon the basin but does not alter the position of the stirrup. There is thus a closed autoclave.

Hamecher's apparatus (Figs. 138 and 139), which is most employed, is characterised by the elimination of explosion risks, and by the care taken in regulating the flame.

It consists of a cylinder supported by three legs and furnished with brackets *c*, which carry the basin *b*, so that the upper edge of the lower half of the basin may be in the same plane as the upper edge of the cylinder. In

order to centre the upper part of the basin upon the lower part, the former carries three wrought iron guides, two of which are narrow and one broad.

The upper half of the basin also carries three guides shaped the same way. The case is constituted of a cylindrical ring, furnished with three handle, sufficiently high to pass over the open basin.

This ring fits into a circular groove on the cylinder rim and forms its prolongation. When the basin is in position its cover exactly fits in the circular envelope. The flame cannot penetrate into the cylinder if the tubes *d* do not allow it to pass.

These tubes are pierced in the cylinder wall, and end at about 1 centimetre below the upper edge of the lower half of the basin.

At the end of 25 to 30 minutes the temperature attains about 150° C. is the cylinder. When the basin and its mantle are in position the thermometer,

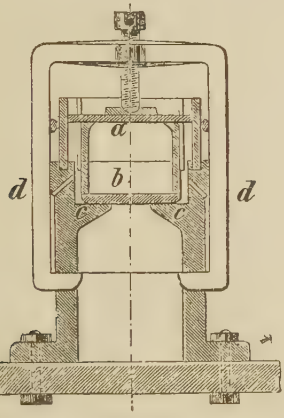


Fig. 138. Hamecher's Gum Plate Press.

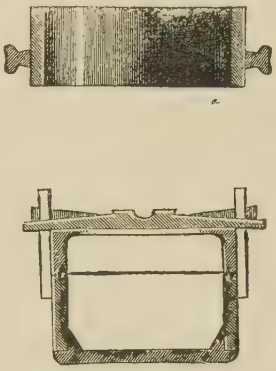


Fig. 139. Basin and Ring of Hamecher's Apparatus.

is introduced, and the flame kindled and regulated so as to surround the whole basin. At the end of about twenty minutes the temperature becomes uniform and the thermometer remains stationary. At this point the thermometer indicates 150° C., and, after removing the thermometer and putting out the flame, the screw is worked rapidly, care being taken that the cover remains horizontal. If the latter is not the case it is unscrewed, the cover displaced from its groove, and the basin moved so that the pressure may be uniform.

The operation lasts from one to three minutes. The hot plaster transmits sufficient heat to the celluloid to soften it, and then an easier working of the screw will be noticed. After a few minutes' interval at this stage, the compression is renewed. After ten minutes' closing of the basin the pressure is released.

If the apparatus has to be used immediately for another operation the basin is removed and cooled in cold water, or by a current of cold water, for half an hour. It is then withdrawn from the press and the mould taken out. The

moulded piece is next finished with the chisel and file, then polished with soap and powdered chalk.

Phonographic cylinders and discs. Celluloid permits of easy impression yielding clear distinct tones, and the cylinders are very durable and light.

In itself the manufacture of cylinders presents nothing in particular, but researches have been carried out especially upon the reproduction of inscriptions.

We will only mention a few processes.

The following is due to M. Lefforts of New York. The surface of the celluloid cylinder is first softened by the action of a solvent such as ether, alcohol, amyl acetate or amyl alcohol, or by a mixture of two of these solvents. This cylinder is then placed in a mould, which presents on its internal face the inscriptions to be reproduced. The mould is surrounded by a hot case, and the whole submitted to the action of combined heat and liquid pressure in a receiver which has been exhausted. The liquid pressure compresses the soft celluloid upon the engraved cylinder, and the traces are reproduced very finely upon it.

In order to reproduce a large number from the original cylinder an electrotype impression is taken from it carrying on its inner face the traces to be reproduced. Other cylinders are next moulded by the action of heat which softens the celluloid, and pressure which applies it to the mould. A large number of cylinders are thus obtained by an economic method, although a slight weakening in tone has been observed.

This defect may be remedied by the following patented process (German Patent 156413) : The celluloid cylinder is coated with stearic acid, a very good engraving being thus obtained possessing very distinct tones. The stearic acid may be introduced during the course of manufacture of the substance.

For the direct inscription of cylinders, Löschner of Prague recommends the action of a solvent such as ether, by immersing in an ether bath or by submitting them to the action of ether vapour, the cylinders having been previously turned, polished and washed. The inscription may then be made direct.

The result of recent experiments is that the purity of tone depends especially on the crystalline texture of the celluloid, and the processes employed should tend to preserve this structure. The following process was invented for this purpose :

The celluloid cylinder is washed with cold water and, after drying, is immersed for twenty-five seconds in an ether bath, this operation being repeated 12, 20, 24 times in an hour. Also it may be subjected to the action of ether vapour for thirty minutes in a closed cask, at the rate of two exposures in a two hours' interval, afterwards being immersed in an ether bath for 50 to 80 seconds.

To obtain deeper impressions the inscribing point may be loaded with a weight of about 50 grammes.

The discs are registered and reproduced in the same way ; they may be rendered more durable by making them from sheet cardboard, or papier-maché, coated with a thin celluloid layer.

CHAPTER VII

BEADS. BUTTONS

Celluloid beads, like buttons, may be manufactured in two ways. Either they are cut to the desired shape from suitable rods or tubes and fashioned from the pieces obtained or simply made by a moulding process.

The latter process presents certain advantages, notably the economy in manual labour, since moulding only demands one or two operations at the most; also there is no waste, which is a consideration of the highest importance. Unfortunately alongside these advantages, the difficulties attendant on the moulding of pieces of such small dimensions have caused its use to be long deferred, and we are even yet in the research period.

BEADS.

Bead manufacture is concentrated at Gablonz (Bohemia), where it constitutes a very important industry. In France they are manufactured at Montville (Société l'Oyonnithe). Both processes are in operation, but the most general is that of cutting at the lathe. It comprises four operations: cutting, boring, turning, polishing.

Cutting. The rods or thin tubes are taken and cut by special machines which are really lathes. Round or oval beads may then be made. If a round bead is desired the rod is cut into sections having a length equal to the diameter of the rod. If an oval bead has to be made the rod is cut to the length desired. The cutting is performed by the circular saw. This saw should naturally be cooled by a cold water circulation, falling drop by drop upon the saw to avoid an overheating, which would produce a decomposition of the celluloid. A lever maintains the rod upon the lathe bench, while another serves to regulate the saw. The length of a bead is determined by a block holder, which allows the advance of the rod by the desired amount at each rotation. As for the lathe itself, it is driven by a pedal worked by the operator, who, with his hand pushes the rod successively to the block holder. By this simple process it is possible for an experienced workman to cut 3000 pieces per hour from rods if the material is supplied and the pieces properly removed.

Boring. The cylinders thus cut are next submitted to the boring operation, by which a channel is drilled through the interior, unless tubes of suitable inner opening have been employed. In the case of rods the boring is done by special machines revolving at great speed. The productive capacity varies according to the length of the pieces, and according to the channel to be bored, from 288 to 864 per hour.

Turning. This operation, destined to give a round or oval form to the

beads, is made upon a lathe. The beads are carried by steel spindles upon which they are turned. If they are to be decorated the same spindles serve. The bearings of the spindle boxes are mounted with much care so as not to occasion oscillation of the pieces during the operation ; what differentiates these machines more particularly is that the work is not executed by a lathe cutter, but by means of an engraving point.

Polishing. The polishing is not done by the ordinary pumice polishing roller, since the operation would present some difficulty. The polish is brought about by the operation of the vapour from a celluloid solvent such as alcohol or acetone. The operation may also be performed by "roulage" (rolling), which consists in making the beads turn at a moderate speed with the polishing agents, such as leather and cloth cuttings, in a rotary drum.

Decoration. Beads may be decorated by various methods, such as incrustation, &c. This work is usually carried out upon the spindles during the course of working the pieces.

The cutting tools differentiate more particularly these machines from ordinary lathes, being different from ordinary cutters which make the celluloid soft and wrinkled.

M. Rudolf Stübling has obtained good results upon umbrella handles by employing special knives, and has applied this principle to beads. He has, moreover, conceived a machine system which has yielded satisfactory results. We borrow the concise description of this machine and process from *Die Celluloïd Industrie* (October 1908).

The machine has six spindles, and allows six beads to be worked at a time. The six round pieces cut in sticks are introduced into the moving machine, and placed under the six spindles designed for the shaping.

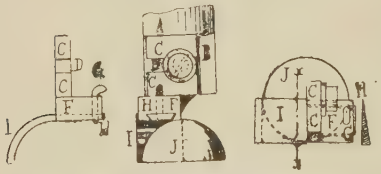


FIG. 140. The Shaping of Beads.

The spindles are lowered automatically, and bore the celluloid cylinders at the same time that the half is shaped. While this operation is being carried out, six new celluloid cylinders are placed into the machine, pass under the spindles and in turn undergo the same operations. A third movement of the machine automatically rejects the beads which have been half bored and shaped. The blocks, therefore, which entered in the form of small cylinders with plane faces emerge in the form of a small cylinder terminated at one side by an hemisphere. The second half is fashioned by repassing the pieces into the machine. They are then turned upon the second half and emerge in their final shape. It only remains to polish them by the action of alcohol vapour, and then to thread the beads upon a fibre by means of a suitable appliance.

The blade *I* has the form of a quadrant (Fig. 140), and by means of a conical cut gives the bead its profile. The blade *I* is prolonged by a prism *H* which is fixed by a pin *G* into the blade carrier *F*. This blade carrier may slide upon a

tool carrier C possessing grooves D. This shaft rests upon the faces B of the cutter carrier A, to which it is fixed by a screw E. The edge of the blade is at any instant exactly in the median plane of the cutter carrier A; sharpening diminishes the width of this blade, and the amount lost is recovered by the lateral displacement of the blade which the grooves D allow.

A dozen different blades corresponding to divers shapes and sizes are set up. When six beads are cut out the pin G is removed, the knife moved, and the machine arranged for recommencing the operation. Figure 140 represents a blade ready for cutting a hemisphere.

M. Rudolph Stübling recommends the following machine (*Die Celluloïd Industrie*, 1908):

The upper part of the frame carries the bearings $B\,B$, in which are secured the six spindles E; upon each of these spindles a small pulley D is placed. The spindles are grooved, and each pulley carries a screw thread J. The extreme spindles on the right and left carry a head F of hemispherical shape. The four intermediate spindles carry rings 2, fixed by six-sided nuts 1. Between each ring 2 and each of the heads F is a special spring arranged upon the spindle E, whose power is sufficient to raise the spindle and maintain it in the upper position. Below the spindle cutter carrier is a cylinder K_1 carried by a shaft l. In this cylinder K_1 is a second cylinder K connected to the first by cast-iron spokes x. The cylinder K rests upon bearings. The points r serve for finishing the beads, and are carried by the pieces s fixed upon a block which connects them. Each of the pieces carries an extension n. The holes through which the points r pass are covered by the plates q, so that only the points r pass. Behind the cylinder K_1 is a channel y in the axis of each spindle, whose depth corresponds to the length of the beads to be obtained. The six channels thus formed are connected by y_2 and fixed to the frame of the machine by a screw y_3. The curvature of the pieces n serves as guide, and the four pins Z of the cylinder K_1 are also guides through the medium of the pieces u and t. The slide P is furnished with a strong point p_2 and upon the same line is another point p_{12}. Between p_2 and p_{12} is a special spring which draws the slide P against $P_1\,P_1$.

The cylinder K_1 turns in the direction indicated by the arrow. Above the frame between the arms C a shaft is arranged carrying the driving pulley and two cams not represented on the Figure. Fig. 141 shows only a portion of cam L. This shaft drives at the same time the periodic movement of the cylinder, which makes four revolutions per minute and remains at rest for 3 seconds at each quarter turn. A rotation lasts nearly 4 seconds, so that with 4 stops of 3 seconds the total rotation period of one cylinder turn is about 16 seconds; the cylinder therefore makes almost four revolutions per minute, and yields therefore $16 \times 6 = 96$ beads per minute half cut, or 48 beads per minute, *i.e.* 2880 beads per hour.

The cams L lower the spindles, which are all moved at the same time by the bridge 3, to which they are fixed by a six-sided nut 1 and a ring 2. During this movement of the cams the cylinder K remains at rest, and the small

celluloid cylinders placed upon the points r_2 are shaped. As soon as the cams d cease to operate the spindles are raised again, and the cutter stops working; then the cylinder K_1 advances by a quarter turn. The points r_1 come in their turn under the cutter carriers; the cams work anew, the cutters are lowered and work upon the beads until the cylinder stops again.

At each turn of the cylinder the pin Z pushes the cam u and the carriage P. Immediately afterwards the spiral spring extends, and the cam t drives back to

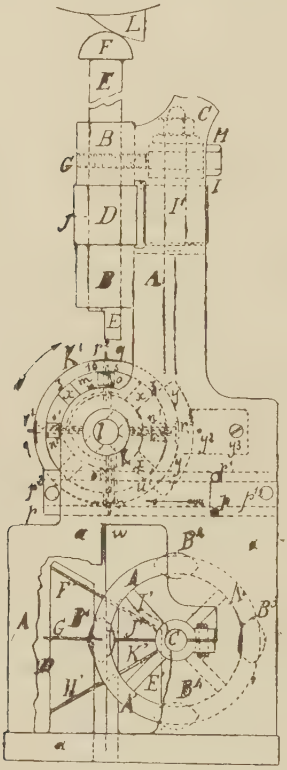


Fig. 141. Bead Machine (Side View).

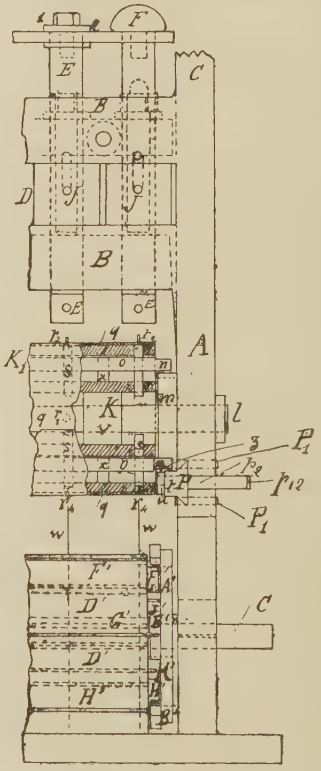


Fig. 142. Bead Machine (Face and Section).

the interior of the cylinder the points s which carry away R_4. The finished beads fall upon the needles w placed directly under each bead. These needles w are maintained between the six needles F' G' H' I' J' and K' situated between the columns D' and E'. The guide F' acts simultaneously with I' G' with J' and H' with K'. The apertures B_1 B_2 B_3 B_4 situated upon the wheel A' allow the beads to be withdrawn from F' and I', G' and J' then from H' and K'.

A small boiler serves for producing alcohol vapour, which is conveyed by small tubes into the channel y where valves only admit it at the instant when the beads pass, these being then acted upon.

For charging the machine with fresh beads, the slips q are removed from the cylinder K_1 and uncover the pieces s. The openings have a diameter greater by 3 to 4 millimeters than those of the largest beads to be obtained.

The moulding of beads. The moulding process consists in softening the celluloid by heat. The plastic celluloid is then forced through narrow apertures so as to form rods of small diameter, which in the plastic state are compressed into bead moulds traversed by an open pipe situated in the axis of the bead, and corresponding to the diameter of the bead hole. Fig. 143 represents an arrangement of this kind for bead moulding. The mould consists of two parts A and B. An amount of celluloid is taken, calculated for filling the mould space and the channel C D.

The form thus prepared is submitted to compression. Two rods F G penetrate in the pipes C and D, pushing the celluloid before them. These rods penetrate as far as the middle of the space where they meet. They carry two holes H I which permit the air to be expelled. The celluloid is thus compressed from the centre towards the periphery of the mould.

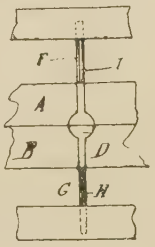


FIG. 143. The Moulding of Beads.

The mould is only constituted of two parts, for allowing the finished bead to be removed. A certain number of moulds of this kind may be arranged side by side, the rods being worked by the same press, and a large number of beads thus produced in a single operation.

This process is very rapid and occasions no waste. A certain amount of care is required for determining the exact amount of celluloid necessary. It is economical, because it requires little manual labour and does not occasion loss of material, but the operation is very delicate and irreproachable articles are obtained with difficulty. The construction of the mould in two parts is an inconvenience particularly great for beads, and the process has long since been abandoned.

M. Rudolf Stübling has conceived a special appliance, whose description we borrow from *Die Celluloïd Industrie* (1908).

The process consists in preparing the shape as before, and compressing it from the centre towards the periphery. The mould is constituted as follows :

It presents a circular section, and is placed vertically, resting upon a foundation provided with a rib w (Fig. 145). This mould in two parts A B is arranged in the middle of the apparatus. The mould has a slightly conical form, and the part which surrounds it is also slightly conical. It is hermetically closed and arranged so that the groove which it carries at its lower extremity may exactly receive the rib w. An absolutely exact position of the mould in the apparatus is thus secured. A channel is provided above by which the mould may be held, transported and placed in position.

As many beads may naturally be manufactured in a single operation as there are chambers in the mould.

In Fig. 145 eight are represented, but there may be 20 or 25 ; the only

limitations are imposed by the working accommodation and the difficulty in obtaining an exact movement for a large number of rods arranged upon an extended length. It is evident, on the other hand, that besides the economy in manual labour which results from a large production in a single operation, the cost of installing an apparatus capable of giving 20 to 25 beads at a time does not grow in proportion to the number, and one installation for 25 beads costs proportionately much less than one for a production of 10 beads per mould. It is the same as regards the space required. The tendency is therefore to construct apparatus for allowing a large number of beads to be manufactured at a time. The plastic celluloid is introduced through the aperture *C*. The rods *q* are pushed forward by the press. The two bodies of the pressure cylinder *J K* are maintained in position by two plates P_1 P_1 (Fig. 144). They are

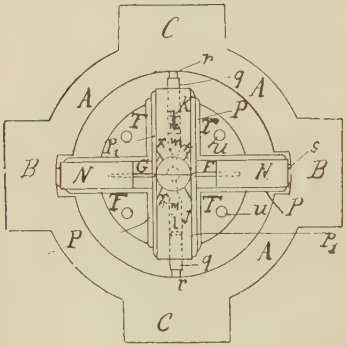


Fig. 144. The Moulding of Beads.

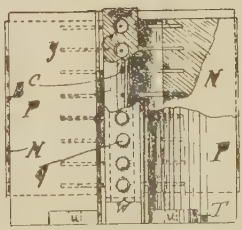


Fig. 145. The Moulding of Beads.

removable, and may be changed according to the dimensions of the beads one desires to obtain.

After sufficient celluloid has been introduced into the mould, the latter is raised above the rib *w* by means of a lever, the celluloid is cut, and the mould is ready for the pressure. It is rotated a quarter turn and replaced upon the base, the rib *w* penetrating into the mould groove. The rods *F* and *G*, after the rotation of a quarter turn, are opposite the channel *C D* which is pierced into the mould and penetrate into it by pressure. The celluloid is driven before them and laterally compressed.

The moulding operation is thus made in two phases. In the first the mould is charged with celluloid by the presses *J K* ; in the second, this celluloid is compressed by the rods *F* and *G* into the mould and worked into a suitable shape.

The whole appliance is maintained in position by set squares *P P P P*, in the spaces of which are placed segments *T* with holes *U* for union by means of guide rods *O* (Fig. 144). Between the pieces *P*, which maintain together the form *A B* of one part and the presses *J K* of the other part, are four channels *x* in which cold water may be circulated as soon as the compression is at an

end. A ring *A* forms a rigid, hermetically closed union. This ring is formed of a piece of hollow cast iron having four projections *B B C C*, in which are lodged the hydraulic elements *r* and *s*. The installation is entirely closed by steam pressure, and only the pressure apertures remain open. The operation over, a circulation of cold water cools the mould and the beads are removed.

A single person can manage several presses.

The principal centre of the bead industry is at Gablonz in Bohemia, which contains about 600 workshops, comprising the works proper and smaller workshops. In reality, work is organised at Gablonz very similar to that of the comb manufacturers at Oyonnax. The work is largely carried out at home, either by one or more families together performing the complete operations or, on the other hand, by one family carrying out only one of the manufacturing processes.

It is very remarkable that the primary material is not manufactured in Austria, where no celluloid works are in existence. More than six million francs' worth of celluloid are imported into Austria every year, and more than half of it is utilised for bead manufacture.

BUTTONS.

Celluloid is naturally well fitted for the manufacture of buttons, taking sufficiently readily the shapes desired for them, not being fragile, and also being very durable; it does not take up moisture or spoil, nor is it too expensive, while it can imitate metals, precious stones and pearls.

For this manufacture many processes may be used, such as lathe cutting as practised for beads, moulding, or stamping from a celluloid plate.

In the first case, small discs having the button dimensions are cut from rods, these being then turned, bored, and finally submitted to the pumicing and polishing operations. This process is applied particularly to buttons which are half-round, conical, or even of more complicated shape. In order to reduce waste to a minimum, rods of diameter corresponding exactly to the size of the button are taken. The cutting is very easily made. The turning apparatus and *modus operandi* are the same as for buttons made of different material. We shall only point out in this place that certain machines allow several pieces to be made simultaneously, as in the case of beads. One of these machines, for example, invented in Austria, permits of cutting, turning, and boring three pieces at a time. Usually the operations of cutting, turning, and boring, are made by separate machines.

Andès [1] mentions a button system composed of two celluloid discs, and a small piece of cloth fastened together so firmly by means of a celluloid solvent plus paste, that the whole is inseparable.

Batonnier and Michel's process may also be applied to celluloid buttons. A paste is formed, and spread upon a sheet of paper or metal to a thickness of

[1] L. E. Andès. *Zelluloïd und seine Verarbeitung*. Hartleben, Leipzig, 1908.

some millimetres. Colours may be added to this paste. The whole is lightly compressed as it is immersed in hot water or placed in a steam chamber, then dried.

The moulding of buttons is carried out as for other celluloid objects. For the flat or round button with holes an appliance similar to those for moulding beads may be employed.

Stamping out presents nothing in particular.

Metal buttons covered with celluloid are also manufactured. This coating is made by the usual process for covering objects with celluloid, to be discussed later.

CHAPTER VIII

CELLULOID SOLUTIONS AND LACQUERS

THE property of celluloid dissolving in acetone, amyl acetate, ether, alcohol, and the mixture alcohol-ether, has been utilised for the manufacture of solutions and lacquers used for coating a large number of objects, for protecting metals, welding celluloid, &c.

Manufacture of the solutions. The solutions are made up in hermetically closed vessels provided with stirrers and heated with steam. The vats of lined wood or enamelled iron, in cylindrical form for preference, are closed by an air-tight cover through which passes a stirrer which works until solution is complete.

The apparatus should be arranged so as to avoid any escape of solvent vapour, these vapours being very inflammable and dangerous to the workmen. The manipulations should therefore be made with every arrangement possible for avoiding the inhalation of vapours by the workmen, and also for removing all danger of fire.

The apparatus should always be in a perfect state of cleanliness, as well as the materials employed for solution, since filtering, which is very difficult and allows a large amount of impurities to pass through, would then be avoided. Straining through wire gauze is often carried out, as we shall notice, for solutions destined for the film manufacture, yet the object of this filtering is not to eliminate impurities but to render the solution more homogeneous. When the solution is turbid it is allowed to rest for some days, when it clears itself.

To make a solution the celluloid is cut into small strips, so as to offer a large surface for the solvent to attack, placed in the vat previously mentioned, and soaked for several hours in the solvent, where it is impregnated and dissolved. The duration depends on the celluloid and on the solvent employed, as well as on the consistency of the solution desired.

Instead of using crushed celluloid, or waste previously cleaned, spongy celluloid may be employed. According to Böckmann the latter is the process employed for the Société Général de Chromolithie at Paris. The spongy celluloid is prepared by submitting freshly manufactured celluloid, which has not been in the block press, to the action of the vacuum. The alcohol evaporates completely in the vacuum, and sufficiently briskly to cause a multitude of small holes in the plate. This spongy celluloid offers a large surface for solvent attack and dissolves rapidly. According to Böckmann it is first digested successively with acetic ether, acetic acid, ether, then in a mixture of alcohol and castor oil, and finally in a mixture of alcohol, amyl acetate, and spirits of turpentine. A lacquer is thus obtained which may be used in the cold.

About twenty-five years ago solutions of celluloid or nitrocellulose were employed for the first time for coating objects. The lacquers obtained are known in commerce under the names of Cristalline, Zapon lacquer, Victoria lacquer, Xyline lacquer, &c.

They have the remarkable property of not giving lustre to unpolished surfaces of wood, paper, tissue, leather, &c., and on the other hand of yielding all their lustre to these surfaces when they are polished. They are invisible, or almost so, and do not modify the aspect of the object's surface which they only protect. On the other hand, every lacquer of resin and drying oils may be easily removed by scraping, and deteriorates under the influence of physical or chemical agents; celluloid lacquers are unattacked by these agents, and by fats or acids, while they even resist scraping. While ordinary resin lacquers deposited upon polished metal iridesce in sunlight on account of their heterogeneity, the former never produce this effect.

Finally, on account of the extremely small thickness of the layer of celluloid lacquer, the object preserves all its suppleness and elasticity.

The advantages of celluloid and nitrocellulose lacquers are therefore unquestionable.

MODES OF APPLICATION.

These lacquers may be applied by four processes, viz., immersion of the object in a bath, application at the pulverisator, application by a spreader, brush application.

We shall describe the first three processes in the paragraphs relating to the manufacture of leather papers, impermeable tissues, and the covering of different objects with celluloid solution. The fourth process may pass with comments.

In England, many wooden and metallic articles are coated with celluloid. This application gives a much better appearance to the wood markings, while it preserves it at the same time from the action of atmospheric agents. The metals are protected against oxidation.

For making this application, the manufacturers of household goods employ a machine by which inlaid work is covered with an exceeding thin layer of celluloid and then polished. This layer may be absolutely transparent, and the polish is much more durable than with ordinary varnishes.

These lacquers are also used for coating wheel rims to protect them against oxidation. Finally the lacquers may be stained either by vegetable or aniline colours. Fairly thick lacquers constitute a true enamel.

Celluloid solutions may be utilised for filling up the pores in wood before polishing, so as to obtain a perfectly level surface and compact texture. In this case a little resin varnish is added to the lacquer, and the coating is made without pressure for better penetration into the wood pores. The fibre is unpenetrated by the celluloid and unattacked.

VARIOUS SOLUTIONS AND LACQUERS.

Innumerable formulæ exist for solutions and lacquers, according to the use for which they are destined.

Those most in use are quoted here without further comment.

Böckmann's Formulæ.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	gr.	gr.	gr.	gr.	gr.
Celluloid	5	10	5	5	5
Amyl acetate	16	30	,,	50	25
Acetone	16	30	,,	,,	25
Ether	16	30	,,	,,	,,
Camphor	,,	4	5	,,	,,
Alcohol	,,	,,	50	,,	,,

Andès' Formulæ.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	gr.	gr.	gr.	gr.	gr.
Celluloid	5	10	5	5	5
Amyl acetate	30	130	,,	200	50
Acetone	30	130	,,	,,	50
Sulphuric ether	30	130	,,	,,	,,
Alcohol	,,	,,	500	,,	,,
Camphor	,,	4	1	,,	,,

A dull lacquer :

Celluloid	80 grammes.
Sulphuric ether	2000 ,,
Alcohol	2000 ,,
Essence of Bordeaux turpentine	750 ,,

Nitrocellulose lacquers :

According to Halle :

Amyl acetate	4 gallons.
Benzene	4 ,,

In this mixture 2·5 English pounds of pyroxylin are dissolved.

According to Wilson :

By English Patent 6061 the nitrocellulose is dissolved in amyl acetate, but according to German Patent 56946, on the same subject, there are dissolved :

Collodion wool	1 gramme.
Dinitrotoluene	6 to 7 ,,

Nitrocellulose lacquers (continued):

According to Bolton:

Pyroxylin	30 parts.
Camphor	10 „
Alcohol	1000 „

According to Böckmann:

Collodion wool	10 parts.
Ether	35 „
Alcohol	60 „

The collodion is digested with ether, the alcohol added, the solution decanted, and 4 to 6 parts of camphor dissolved in it.

According to Eckstein:

Collodion wool	8 to 10 parts.
Ether or alcohol	100 „
Castor oil	2 to 4 „
Resin	4 „

The operation is carried out as above.

According to Gérard:

Gelatine	1 part.	
Trinitrocellulose	2 „	dissolved in glacial acetic acid.

There are added:

Acetic ether	19 parts.
Castor oil	a small quantity.
Gumlac	„

According to Tscheuschner:

The cellulose from nitrated cotton is dissolved in ether and alcohol, with the addition of boric acid.

According to Bonnaud:

There are mixed together a cold solution of copal resin in castor oil, and a nitrocellulose solution.

According to Grane:

Pyroxylin	2·5	parts by weight.
Amyl acetate	40	„
Benzene	40	„
Methyl or ethyl alcohol	20	„

The amyl acetate may be replaced by butyl acetate or propyl acetate.

According to Andès:

Good results are obtained with the following proportions:

Nitrocellulose	100 parts.
Amyl acetate	150 to 400 „
Amyl alcohol	150 to 400 „

For the pyroxylin solution 1 part is dissolved in 40 parts of camphorated alcohol.

Or again:

Pyroxylin	5 parts by weight.
Methyl alcohol	32 „
Amyl, butyl or propyl acetates	10 „
Amyl alcohol	32 „

Or:

Pyroxylin	10 parts by weight.
Camphor	5 „
Amyl alcohol	16 „
Methyl alcohol	44 „
Propyl or butyl alcohol	20 „

Or again:

	No. 1. Parts by weight.	No. 2. Parts by weight.
Nitrocellulose	40	10
Cedar oil	20	2
Amyl acetate	40	30
Amyl alcohol	„	25
Benzene	„	3

Celloidine Lacquers:

	No. 1. Parts by weight.	No. 2. Parts by weight.	No. 3. Parts by weight.	No. 4. Parts by weight.	No. 5. Parts by weight.
Celloidine	5	10	5	5	5
Alcohol	„	„	50	„	25
Amyl acetate	16	30	„	50	25
Acetone	16	30	„	„	„
Ether	16	30	„	„	„
Camphor	„	4	0·5	„	„

Coloured lacquers :

There may be taken :

Pyroxylin	3 to 4 parts.
Boric acid	1 „
Resin	25 „
Mineral colour	20 „
Alcohol-ether	100 „

Or :

Collodion mixed with 2 or 3 per cent. acetone.
Camphor, 1 per cent.
Aniline dye.

Insulating lacquer for protecting wood and metal. The nitrocellulose, with a calcium chloride solution, is dissolved in amyl acetate, alcohol, ether, &c. For utilising this lacquer the object is coated with vaseline or lavender oil, and then the lacquer put on.

Heavy black lacquer. This lacquer is especially used for wood and has the following composition :

Celluloid, 850 grammes softened in 1·700 kil. of very concentrated alcohol. It is dissolved in 19 kilogrammes of acetate and the solution clarified by standing is coloured with :

Nigrosine	115 grammes.
Lamp black	425 „

Lacquer for covering impressed celluloid :

Copal dried at 100° C.	6·48 parts by weight.
Alcohol	16·40 „
Water	1·20 „
Ether (specific gravity 0·725)	75·47 „
Essence of turpentine	0·45 „

Lacquer for invisible pyroxylin :

Celluloid	20 grammes dissolved in	
Acetic acid	100 „	solution clarified by
Methyl alcohol	120 „	

This solution poured over a glass plate gives a good appearance of white enamel. It is clarified by 250 grammes of methyl alcohol.

Also there is dissolved :

Collodion wool	10 grammes in
Methyl alcohol	100 „

The white snow obtained is dissolved by clearing with ethyl alcohol.

Or 100 grammes of a solution of collodion in alcohol-ether mixture is diluted with 100 grammes acetic acid.

THE VARNISHING OF IMITATION PEARL WITH CELLULOID.

The ease with which pearl may be imitated by celluloid has been employed for recovering false pearl with a coating of this substance. The pearls are immersed in a solution of celluloid or nitrocellulose lacquer, and then dried. The celluloid layer may be transparent and colourless, and allows the surface of the false pearl to appear, which has been previously coloured to imitate mother of pearl. The layer may itself be coloured or finally the pearl, coated with celluloid, may be immersed in a dye bath.

The baths most current, contain about $\frac{1}{4}$ per cent. of colour. Andès quotes the following bath for obtaining a good golden shade:

Alcohol	100 litres.
Alizarine yellow	120 grammes.
Alizarine red	80 „

CHAPTER IX

THE COATING OF OBJECTS WITH CELLULOID

IMPERMEABLE TISSUES—IMITATION LEATHER—COATING BY A CELLULOID SHEET—HOOKS AND CLASPS.

Among the processes employed for imitating fancy goods made of mother of pearl, ivory, tortoise shell, rare woods, &c., or to render objects impermeable or insulated by means of celluloid, figures the covering of these objects by a thin sheet or layer of celluloid. Buttons, also hooks and eyelets of footwear, are frequently of metal coated with celluloid. Dolls are often of porcelain or other material covered with celluloid to give a good appearance and render them less fragile; the handles of sticks and umbrellas are often of wood recovered with celluloid. In electrotechny, wires and other objects are insulated by a celluloid coating. We have seen that tissues and papers may be impregnated. Finally, a very large number of varied objects are coated with celluloid.

This covering may be made by several processes, such as immersion in a solution or by spreading on the solution by means of a sheet or tube. The latter procedure is employed for stick and umbrella handles as previously noticed; recovering by a sheet is much employed for the hooks and eyelets of footwear. Recoating by immersion in a solution is also employed for a large number of objects, particularly for wire, dolls, hooks and eyes, tissues and artificial leathers. For the latter the process of deposition by a spreader or pulverisator is most usual.

COATING BY IMMERSION.

This process is specially employed for wire. For this purpose a strong solution of amorphous celluloid or of pyroxylin dissolved in amyl acetate, acetone or alcohol is used, the solvent being afterwards evaporated.

The object, *e.g.* wire, is fixed upon a drum, which is made to revolve in a vat filled with solution. The operation over, this drum is replaced by another and so on. Each drum is then taken into a drying chamber, where the object is dried and solvent evaporated and recovered by condensation.

To coat a doll's head for example, it is immersed in a celluloid solution, then dried as before. The doll's head thus possesses all the advantages of celluloid without its defects.

The liquid layer may be deposited by means of a brush, this being a varnishing process.

Covering by a sheet is made either by hot compression or by drawing. The core to be coated is manufactured, and in order to cover it by the drawing process a strip of celluloid is taken of great length, which is immersed in a hot liquid to soften it a little, then extended upon the object by drawing out and afterwards chilled in a cold bath.

Sheet covering is usually made by compression.

IMPERMEABLE TISSUES—ARTIFICIAL LEATHERS.

Celluloid is much employed for rendering cloth and paper impermeable, and for imitations of leather such as papers, pegamoid, loréïd, dermatoid, glorid, &c.

For this purpose cloths or papers are covered with a celluloid solution, which hardens by evaporation of the solvent and forms a thin skin or pellicle upon the cloth or paper, rendering them impermeable, and imparting lustre. By hot rolling, patterns in relief are obtained upon leather papers.

These various products may be classified into three principal groups: impermeable fabrics, imitation leather and papers of all kinds, electrical insulating materials.

IMPREGNATION.

Pegamoid is soft and admits very well of being worked up; its appearance is at least as good as that of the best leather; for furniture it has the great advantage of being washable, even with tepid water; it resists acids and fatty substances; finally, it is supple, while its strength is even superior to that of leather. It may be advantageously used for covering furniture, and for rendering covers washable, capable of resisting moisture and unstainable. It is capable of extensive decoration.

In principle, this manufacture consists in coating paper with celluloid, either by compression or otherwise, and stained or unstained, also for woollen fabrics more or less thick and generally in the form of flannel. The tissues should be prepared so as to be capable of absorbing the solution.

The latter is of variable consistency according to the object desired, the mode of application, and the addition of colours or not. Solutions of celluloid or nitrocellulose are used to which castor oil, caoutchouc, oils, &c., may be added for imparting greater suppleness.

The solution in the liquid state is added to that destined for imparting colour. The operation of impregnation is made by means of the spreaders employed in the manufacture of india-rubber fabrics, and the coated tissue or paper is then taken to the drying chamber or to the stove, regard being paid to the fact that the solvent vapours are very inflammable.

Celluloid is dissolved in acetone, amyl acetate or alcohol, so as to obtain a solution very consistent but still fluid.

Andès quotes the following solution :

Celluloid	10	parts by	weight
Alcohol	30	,,	,,
Amyl acetate, acetone, &c.	100	,,	,,
Alcohol	50	,,	,,
Castor oil	3	,,	,,

On account of inflammability the solution is made up in vats of enamelled iron or wood, provided with stirrers and carefully closed.

The best is the cylindrical form with an aperture for filling which may be closed by a cover, and an orifice for running off the liquid. The cover should

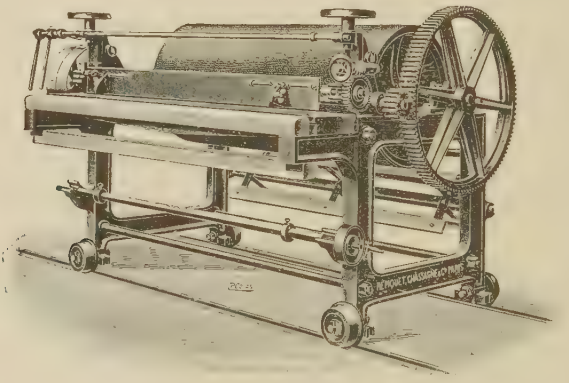


Fig. 146. Repiquet-Chassagne's Machine for Coating.

be removable and ensure hermetic closing. The stirrer is worked as long as the celluloid is not completely dissolved.

It is obvious that the vat and stirrer should be perfectly clean, and the solution absolutely freed from extraneous substances, so as to avoid filtering the solution. Filtering, indeed, presents great difficulties, and may only be carried out imperfectly, a large part of the extraneous substances remaining with the solution.

When the solution is made up, the application is made by the spreader. Before operating, the apparatus is adjusted so as to obtain the desired thickness of layer upon the paper or fabric after drying. A thickness of 0·2 to 0·1 millimetres of solution is sufficient for ordinary purposes. The adjustments of the cylinders, and of the blade, should therefore allow for obtaining such a thickness. The paper or fabric is taken in the ordinary way so that it is covered with a uniform layer, then passed to a drying table, or, better, to a stove chamber heated between 30° and 36° C. and situated behind the cylinders, so as to evaporate a portion of the solvent before suspending the fabric or artificial leather in a drying chamber at a temperature of about 35° C. The drying before passage to the drying chamber should be sufficient to prevent any obscuring or watering

upon the surface of the layer. Fig. 146 represents a machine for coating made by Repiquet-Chassagne. In addition to the cylinder there is a drying table or stove not represented upon the diagram.

The stay in the drying chamber is determined by the time necessary for the layer to acquire the consistency desired. According to the circumstances an average of four to five hours is necessary. In these manipulations great precautions must be taken against the inflammability of the solvent vapours and their inhalation by workmen. In the apparatus shown, the stove which accompanies the cylinder, and is not represented in the Figure, is completely closed. It may be surmounted by a vapour condenser.

When the celluloid layer is to be exceedingly thin, a liquid solution should be employed and spread out by spraying upon the fabric.

Fig. 147 represents a sprayer of this kind. The solution is contained in a copper receiver *A*, into which it is conveyed by the pipe *B*. The apparatus

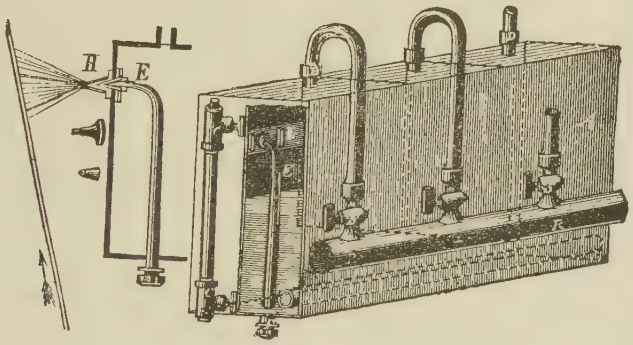


Fig. 147.

carries at the side a fluid gauge *C*, analogous to gauges of water level. The receiver comprises a number of compartments, which may be worked simultaneously or separately according to the width of the fabric to be coated, the apparatus having a length equal to the greatest width of the fabrics or of the parts to be coated. The lower parts of these compartments are in communication, while the upper air chambers are separated, and each possesses an air pipe, which may be placed in communication with a large air conduit by means of a tap *R*. On the other hand, each compartment is furnished with a pipe *E* terminated by an apparatus which sprays the liquid in a fine shower upon the fabric or paper to be coated. This pipe *E* is served by the openings *C*, through which the liquid may pass out, and which also open into the air channel. The apparatus which is screwed on at the extremity of the pipe *E* is conical, and round it is fitted another of greater diameter *H* fixed to the wall of the vessel. In the air chamber on each side of the sprayers are slits *L* by which compressed air passes into them.

One or several compressors force air into the receiver.

To use the apparatus, as many of the taps *S* are opened as the width of the fabric or paper to be coated demands compartments, and the compressed air presses the liquid mass and forces it towards the sprayer through the pipe *E*. Also this compressed air penetrates into the sprayer by the slits *L* and divides the jet, which in the form of a fine shower is forced upon the material to be impregnated. The latter is placed upon two slowly rotating cylinders. According to the air pressure and the rate of movement of the fabric, a layer of celluloid more or less thick is obtained.

This process is more particularly employed for covers and fabrics. It permits of easily graduating the thickness of the layer.

Lilienfeld's process. A solution is employed made up of nitrocellulose or celluloid, 100 parts; ethyl, methyl, or sebacic ether, 40 to 50 parts. The whole is dissolved in amyl acetate, &c.

This solution is spread upon the fabric as a dressing. It has the advantage of imparting a beautiful lustre to the coated fabric.

Guillet's process. The solution employed is composed of vegetable fibre, castor oil, and nitrocellulose, dissolved together in acetone. As an example, 80 parts fibre, 15 parts nitrocellulose, and 5 parts castor oil are used. Some caoutchouc or resins may be added to the acetone, and the castor oil replaced by another oil.

Bensinger's process. About 10 parts of nitrocellulose are dissolved in about 50 parts of wine, with the addition of acetic acid, ether, or other celluloid solvent, 3 parts of oil being added to it. The object or fabric to be impregnated in this solution is immersed for two to three minutes, then withdrawn and allowed to drain. The pores are charged with the solution, while the fabric becomes tough and would be useless in this condition. To render it supple it is placed between two plates of polished metal covered with a thin layer of oil, and submitted to hot compression. The oil penetrates into the pores, and imparts suppleness to the fabric, which is afterwards calendered. The nitrocellulose may be replaced by a solution of celluloid waste.

The Publishing, Advertising, and Trading Syndicate's Process. The fabric is first of all steeped with a dilute celluloid solution, then with one more concentrated. By the addition of about 1 to 2 per cent. oil to the first, and from 5 to 8 per cent. oil to the second solution, sufficient suppleness is secured to the fabric. The first solution, for example, may have the consistency of olive oil, while the other may have that of treacle. The fabric is thus very compact, the whole possessing a very supple surface.

DECORATION.

Whatever may be the impregnation process employed, it may be followed by the decoration of the articles thus obtained with patterns in relief in the case of paper or of imitation leather, pegamoid, loreid, glorid, dermatoid, &c. The operation is made by calendering.

The fabric or leather paper is passed between two slightly heated cylinders

bearing patterns in hollow and relief, corresponding to the relief and hollow of the design to be obtained.

Fig. 148 represents a calender of this kind constructed by the firm Repiquet Chassagne of Paris, and more especially destined for making borders on wall-papers.

Impregnation by brush or by immersion. We can only mention the processes of impregnation by depositing a thin layer of solution by means of a large brush or by immersion.

Recovering by celluloid sheets. Finally, papers or fabrics may be rendered impermeable by covering them with a thin celluloid layer from 0·2 mm. to 0·1 mm. thick.

Hooks and eyelets of footwear and fasteners. Hooks, eyelets and fasteners may be coated with celluloid by immersion in a solution or varnish,

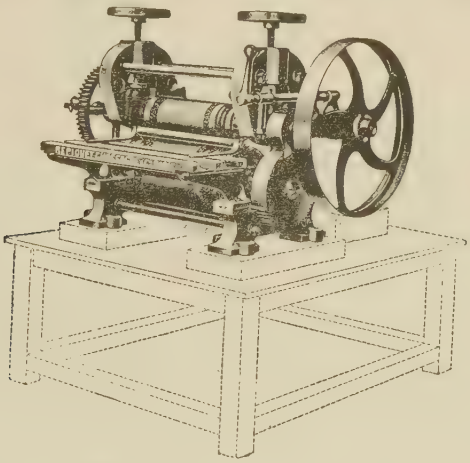


FIG. 148. Goffering Machine for Leather Paper (bordering).

but this varnish is not durable and scales off easily. Coating by a thin sheet is therefore preferable since this may be made thick and durable.

Many processes are in use for this purpose.

Heinrich Vogel's process. The coating is made in the press. What characterises the appliance is that the same operator may manage a large number of presses at the same time. A group of presses is connected to a pressure accumulator by a supply pipe. The presses are also served by an evacuation conduit. Each of these is furnished with an operating lever. The work consists in placing the pieces in the press by commencing at one end and successively manipulating the lever. If the number of presses has been properly calculated for the operation, the first compression should terminate when the operator arrives at the last press. He then returns to the first and works the levers in the reverse direction, removes the pieces, replaces them by others prepared in advance and recommences the operation.

Such is the method involved in a complete operation. The pieces and their arrangement vary according to the processes employed.

Koch's process. The following process is due to M. Koch of Frankfort (Ger. Patent 138006).

A celluloid plate is pierced with holes, which correspond to the small diameter of the eyelet, and this is placed upon a matrix furnished with points

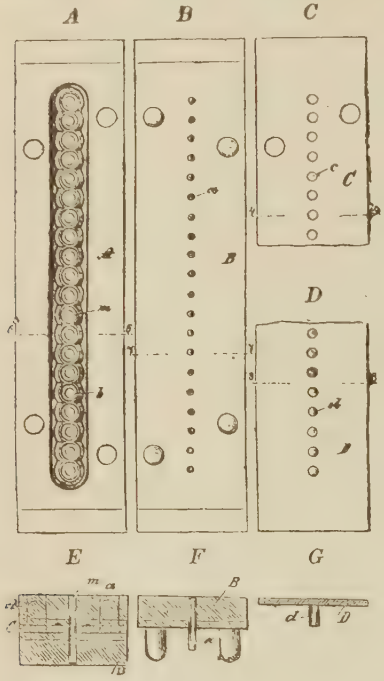


FIG. 149. Koch's Process.

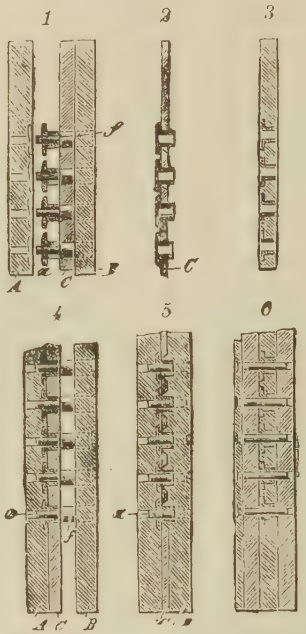


FIG. 150. Koch's Process.

which pass through the holes (Figs. 149 and 150). Upon this plate a second is placed pierced with holes, whose diameter is the external diameter of the eyelet. When the plates *A* and *B* are placed upon each other and upon the matrix so that the holes and points correspond, the whole then being heated and compressed, the celluloid goes into the annular space made by the points in the holes. According as eyelets with a single rim or two have to be obtained, the points of the matrix are caused to mount more or less high, and in the second case a third plate is employed which gives the desired form to the bordering material.

Fig. 149 represents the arrangement; *A* is a view from above, *B* from below, *C* the centre plate, *D* the perforated celluloid plate and *E F G* sections.

The matrix *A* carries a row of points *a* of diameter equal to that of the eyelet exterior. Each point is surrounded at its base by a groove *b* having the shape of the eyelet rim. The plate *C* forms a matrix of two sections, the line of separation being formed of a series of lines alternately straight and

semi-circular, the latter forming, when both parts are brought together, circular holes with the diameter of the eyelet. These two halves are fixed to the covering plate *B* by pins. The guiding of the plates *B* is obtained by points penetrating into the openings *c*.

The operation is conducted as follows:

The punch forming plates *B*, and the covering plate, are separated from that serving as base, and upon the latter a sheet of perforated celluloid is placed. The plate *B* is then applied with the punches enclosed. The whole is taken to 100° C. and submitted to compression. The celluloid slips away to form a ring round the points in the spaces *b*, and passes above the empty space between the points *a* and the space *b* until it arrives at the covering plate. The plates are then removed and cooled in a bath of cold water.

The process may be simplified by using only two plates as follows (Ger. Patent 138571).

The stamping of holes in the plate into which the points penetrate is made separately.

The moulds are perforated at their centre by holes *m*. The middle plate *C* is furnished with holes *c*, and in a single piece. Upon the plate *D* the points *a* may penetrate into the plate *A*. A sheet of celluloid is placed upon the plate *A* and the other plates then arranged one upon the other. The operation is made as above. When these plates are separated, the eyelets remain in the middle plate. The points *d* then penetrate inside and form a hole of greater diameter.

Lacing eyelets. This eyelet may be manufactured by Kaspar Engels' process of Barmen. It is formed of a cylindrical or slightly conical metal core and cut in dovetail. By stamping this metal is encased in celluloid forming a rim. The dovetail prevents the celluloid from slipping.

Buttons by pressure. Hooks corresponding to eyelets are formed by enclosing the head with celluloid by a stamping process. The process of Kempf and Co. of Crefeld may be employed, which consists in making a metal eyelet and forcing over it a celluloid eyelet.

CHAPTER X

THE USE OF CELLULOID IN PHOTOGRAPHY

PLATES AND FILMS.

Celluloid is much employed in photography, either as plates or films. It may form rigid supports capable of replacing glass and not possessing its fragility. With regard to films, celluloid is especially suitable for this purpose, on account of its transparence and suppleness.

PLATES.

The honour of first recommending the use of celluloid for photographic plates belongs to MM. David and Tailfer, while M. Planchon of Lyon was the first who manufactured them. The first plates were self-supporting (autotendues), and were constituted of a celluloid sheet surrounded by a metal frame, which ensured their rigidity and avoided warping.

At the present time thin transparent sheets are employed for photographic plates or thick ones. The thin sheets are generally stained white or rose. The

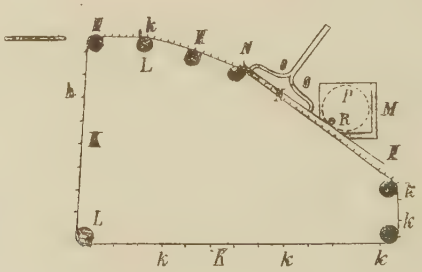


Fig. 151. Continuous Machine for laying Emulsion on Plates.

thick sheets have the appearance of opal glass, and their surface may be polished or not. They are usually cut from celluloid blocks at the planing machine, and their surface is polished in the press to remove the traces left by the cutting operation. These plates serve most often as a block upon which to transfer images in carbon or collodion.

The photograph may be transferred to a celluloid plate in the following manner (French Patent 365604).

The photograph is immersed in acetone, then withdrawn and applied without allowing it to drain upon a celluloid sheet, which may be transparent and polished on both its faces, as in the case of imitating enamel. By means of a

wooden scraper the air bubbles are removed, and the sheet allowed to stand for about two hours; it is then immersed in cold water. Afterwards the paper is removed by rubbing with a cloth which has been soaked in water. The acetone produces adherence to the celluloid, and the paper separates.

These plates may also be used directly for blocks, by coating them with an emulsion of brom- or chlor-gelatine, and employing them as ordinary plates.

FILMS.

Under this name are included very thin sheets of great length covered with an emulsion of silver chloride or bromide and used in photography.

These bands have a width of 35 millemetres, an average thickness of $\frac{13}{100}$ of a millimetre, and they extend sometimes for many hundred metres. They are perforated on either side by holes into which pass the prongs of the cinematograph apparatus. The rapid development of the cinematograph has caused an enormous extension to the manufacture of these films, and the Kodak firm, for example, produces about 100,000 metres per day.

For the manufacture of these films, collodion, celluloid, viscose, or the uninflammable cellulose acetates are employed.

Celluloid offers certain advantages, viz., suppleness added to strength, transparence and permanence to moisture. It presents the disadvantage of containing camphor and nitrated products, which act on the silver salts and impair the sensitiveness of the silver bromide with appreciable rapidity. After some months a celluloid solution may have lost a part of its sensitiveness.

In a general way the conditions to be realised for a film are the following: (1) Suppleness; (2) Tenacity; (3) Transparence; (4) Permanence towards water; (5) Uninflammability.

Celluloid fulfils the first four conditions well; but the fifth it is naturally not satisfied, and that is the cause of so many researches instituted with the object of replacing celluloid by cellulose acetates, work which will be discussed in the chapter on celluloid substitutes.

From the standpoint of strength, a celluloid film is sufficiently strong as to pass a large number of times through the apparatus without the perforations being destroyed.

Celluloid may be employed in two ways, either by allowing solutions of celluloid or collodion to harden, or by cutting thin celluloid sheets. Up to the present the former method has been almost entirely used.

The celluloid should be of special quality. A portion of the camphor has been replaced by castor oil to render the celluloid more supple and to avoid the defects of camphor, but the films obtained turn yellow and rapidly became brittle. An oil content of from 3 to 6 per cent. of the dry pyroxylin should never be exceeded.

SOLUTION OF THE CELLULOID.

For the manufacture of celluloid films it is usual to employ nitrocellulose made from cotton nitrated with 11 to 12 per cent. of nitrogen and sometimes more. The nitrocellulose should be carefully washed. Haddon attributes a proportion of the defects of celluloid to insufficient washing, owing to the presence of acids. This celluloid should therefore not be brittle, be absolutely neutral, and not emit nitrous fumes to obscure the emulsions.

A camphorated collodion is made by dissolving the nitrocelulose in a liquid containing 12 to 25 per cent. of camphor. This solvent is usually a mixture of alcohol and ether, to which may be added amyl acetate and amyl alcohol.

A mixture of this kind with 0·5 to 1 per cent. of amyl alcohol is used by the Kodak firm. La Société Lumière does not employ amyl alcohol. The object of the latter is to prevent the polish being removed. Celluloid dissolves relatively better than collodion in the alcohol-ether mixture.

The collodions thus obtained contain ordinarily from 15 to 20 per cent. of celluloid (camphor mixed with nitrocellulose). They have a viscosity varying according to the celluloid content.

It is of paramount importance that the celluloid employed should be homogeneous, perfectly clear, and free from extraneous matters. Celluloid such as is obtained by solution contains unnitrated fibres, impurities, and portions of varying consistency. It is filtered to render the division homogeneous. This filtration is made under pressure into a receiver by traversing a series of wire gauze.

CASTING.

The celluloid is then made into films by two different processes, viz., casting upon a table or upon a continuous machine.

Casting upon a table. The celluloid solution is poured upon a glass plate or slab of polished glass, surrounded by a border of stiff paper or thin sheet iron to retain the solution.

These glass plates are first carefully cleaned with jeweller's red and alcohol before each operation. They are well dressed, of uniform thickness, and perfectly plumb upon the table whose horizontal position is checked by a water level. The position of the glass plate is itself tested by the level so as not to have to raise certain parts with wedges. The solution, in a liquid state of moderate consistency and perfectly pure, is then spread as a thin layer upon the glass.

This process is very simple but requires a very pure solution and a thoroughly clean apparatus. The rooms in which the casting is performed should be absolutely dust free and well ventilated. The vapours of very volatile solvents should be expelled as rapidly as possible or be absorbed. It would be best to recover them, since these solvents constitute at the same time a considerable

danger and expense. The tables may be covered with a sheet iron lid so as to form an air-tight box, upon the walls of which the solvents are deposited, condensed, and may be recovered, but this arrangement is not without inconvenience, and the recovery presents certain difficulties. The casting is made by means of a draw-plate (*filière*). The solution is poured out, the glass plate moved a little, and the solution allowed to rest and harden. The duration of hardening depends on the thickness of the layer and the nature of the solution; it may vary from a few minutes to several hours. The hardening may be accelerated a little by aiding the evaporation of the solvent with heat.

The film detaches itself when cooled, and if it has been heated the separation is brought about very rapidly by transporting into a cold chamber. If the film adheres too much at the edge of the glass, it is detached on the short side with a knife and raised by means of a smooth ruler from this side.

The film is next dried upon a level table, the face resting upon the glass uppermost. Care should be exercised in not removing it before the necessary time, since the film would be obscured.

This process was the first to be employed, and is still in use with some modifications in detail. Planchon's process utilises a spreader for the casting operation, formed of a type of box possessing near the bottom an aperture of adjustable width regulated by means of a movable plate with bevelled edge. The solution is forced through this narrow aperture, which only allows the slightly consistent solution to penetrate with difficulty, by means of an automatic piston. This spreader is mounted upon a carriage which travels upon the glass plate. The solution flows upon the plate, and the regulated spreader limits and makes uniform the thickness of the layer. Immediately after casting, the glass plate and film which it supports are covered by a lid so as to avoid the deposition of dust.

This process, though simple, does not admit of a very large output, and only permits films to be manufactured slowly with a breadth of 0·50 m. and a maximum length of 50 metres.

Casting by means of a continuous machine. This process permits films to be cast of indeterminate length. The principle is as follows: the solution is run out in a continuous manner upon an endless band driven by a forward motion, or upon a drum of great diameter having a very slow rotation. The film formed is dried and hardened in its course under the influence of a ventilation which expels the solvent; it is then detached from the endless band and carried to a drying chamber. The endless cloth or the cylinder replaces the glass plate and should in consequence possess a well-polished surface.

A large number of different appliances have been invented, which are all derived from the American patent of Stevens and Lefferts (1896).

The solution is run out by means of a spreader upon an endless moving band. This band moves slowly, so that the solution may be uniformly spread at a convenient thickness, regulated on the one hand for the discharge of the spreader by means of the movable blade, and made uniform on the other hand

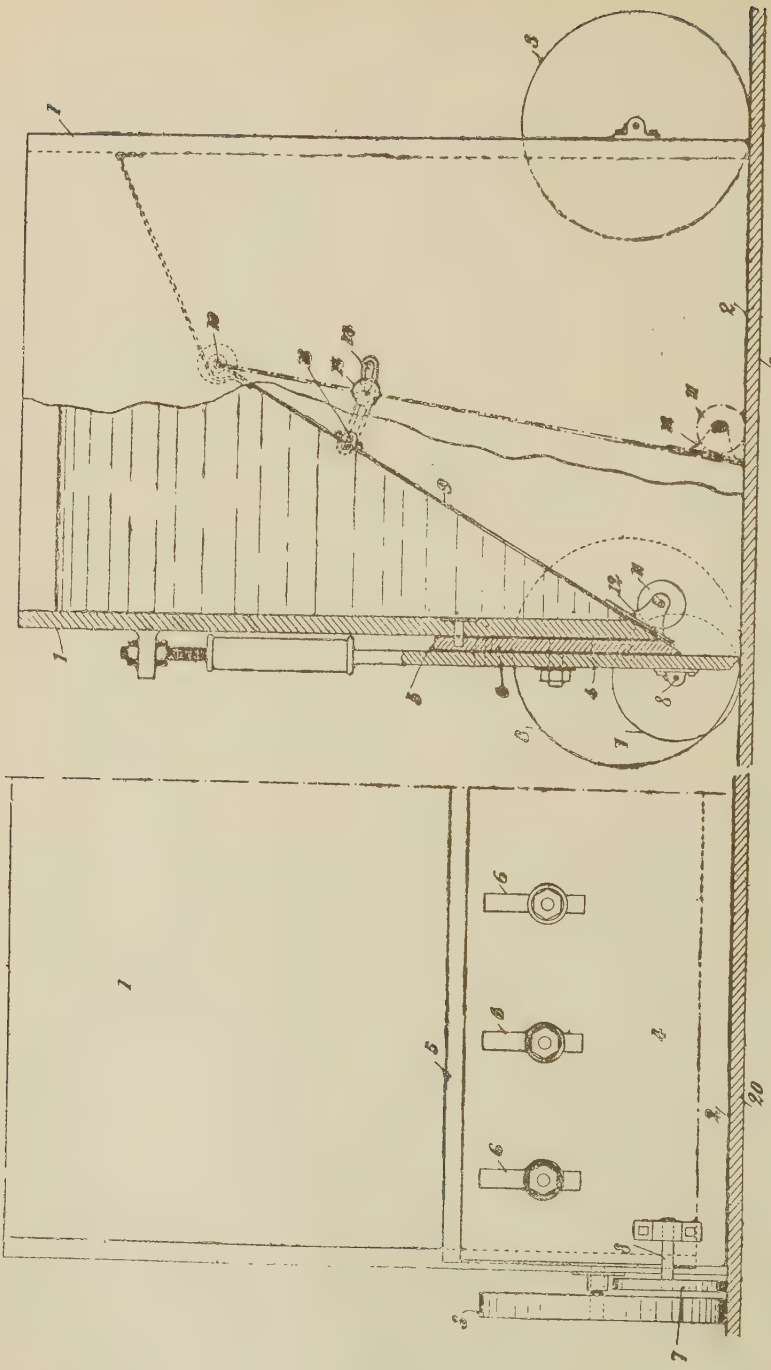


FIG. 152. Soulier's Spreader.

by the regulator attached to this, and in such a way that the film may have time to dry and harden. A ventilation pipe facilitates evaporation of the solvents and the hardening, and allows the solvents to be recovered. Detached rollers next take the hard film and transfer it to a drying chamber.

The bands are of polished metal, of which the best is nickel.

One of the most recent appliances is that of Soulier (French Patent 401795).

Fig. 152 represents the spreader, and Fig. 153 the whole appliance.

We shall describe a typical form of spreader.

The discharge box or spreader 1, is carried laterally upon the endless band 2 by the wheels 3; the anterior part of this box is provided below with a knife 4, gliding the length of a knife carrier 5 in the channels 6, which regulate the thickness of the layer.

The lower part of the blade 4 is maintained at a constant adjustable distance from the endless band by means of small rollers 7, whose axles are carried by

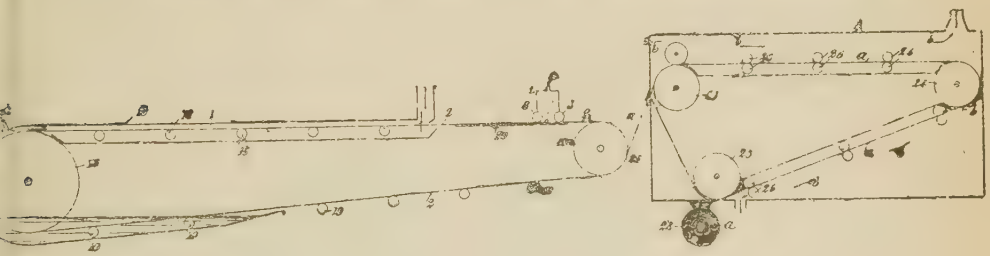


FIG. 153. Soulier's Continuous Casting Arrangement.

the blade 4. In the interior of this box is an inclined partition 9, attached by hinges or by a horizontal axle 10; the lower part of this partition, which constitutes the provisional box bottom, is provided with rollers 11, arranged to carry the endless band 2 when the partition 9 has been conveniently removed from the vertical anterior wall of the box 1. The partition 9 is furnished with a triangle 13, running in the groove 14 by a guide fixed to the exterior of the box 1; by pressing the milled button 15 fixed upon the triangle 13 against the guide 14, the partition 9 is arrested in its rotation about the axis 10, and the separation of this partition with regard to the anterior wall is thus regulated.

This inclined base facilitates the separation of air bubbles, or of gas which may be incorporated in the solution, and its mobility permits of delivering to the endless band a regular sheet of the solution without the air being incorporated in it anew.

The walls of the box 1 may be hollow so that a hot liquid may circulate therein, such as water, steam or vapour, to maintain the fluidity of the solution.

The endless band 2, well polished on the contact surface upon which the plastic material is distributed, is constituted either of a polished metallic band, or by one of metallised gelatine, or of a fabric rendered impermeable and

varnished like oilcloth. This band is rolled up about two drums 16 and 17, one of which is driven so as to communicate a continuous but slow rotation to them; it is supported from place to place by small rollers 18, 19; the lower rollers 19 only support it at the sides, in order not to carry the band of plastic material adhering to the endless band 2.

At the place where the discharge takes place, and upon a certain length beyond the fixed box 1, the band 2 rests upon a flat well-dressed table 20 called the work-table.

The solution discharged on 20 is carried away by the slow continuous motion of the band 2; after having travelled over a part of the drum 16 it

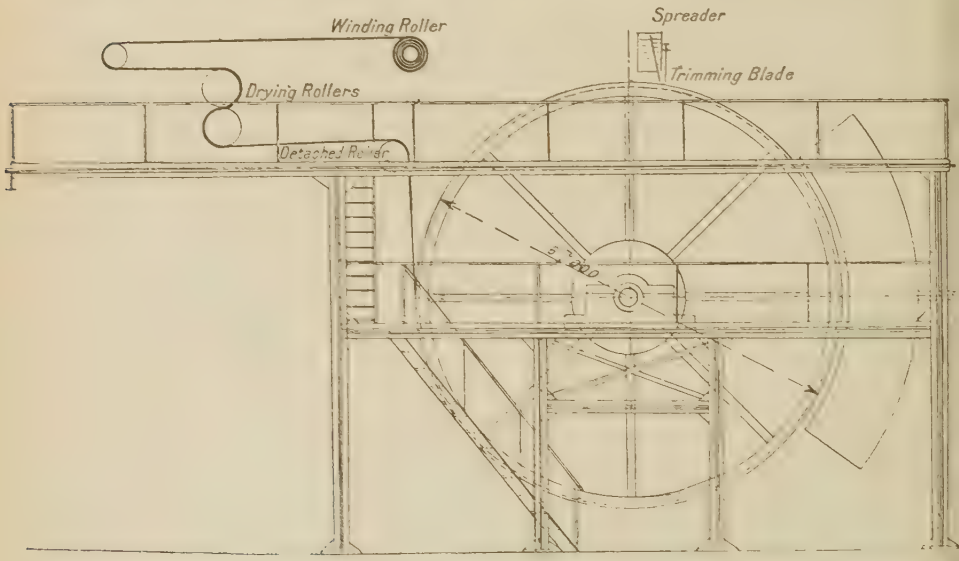


FIG. 154. Appliance for Continuous Casting upon a Drum.

plunges into a vessel 21 filled with a coagulating solution, water, for example, in the case of celluloid films.

The material carried by the band 2, after emerging from the receiver 21, is detached from its support upon the roller 22 and conducted to the drying chambers, where it passes over the roller 23.

To avoid contact of dust with the band, the course travelled by the endless band 2 is protected by a case *B* in which air, which has been previously filtered and dried, is caused to circulate above the band according to the arrows *a*.

The celluloid band *a* is directed into the drying chamber by the rollers 23, 24, 25 and carried between the rollers 26 into a tunnel *A*, in which circulates a rapid current of previously dried and purified air. The band proceeding from the drying chamber is rolled upon a small drum 28.

Drum machines. The endless bands or belts may be replaced by drums of

very great diameter, 6 metres for example, upon which the spreader discharges the solution on the upper part. The layer is made uniform by a trimming blade. Upon one of the cylinder sides an evaporating chamber is fixed, connected with an aspirating ventilator. The cylinder heated to 26° or 28° C. rotates at a very slow rate, one to two turns per 30 minutes for example, according to the diameter, and it may be warmed by central heating as in Flintsch's apparatus or by lateral heating. The slow rotation of the cylinder and its large diameter compels the film to have a path of sufficient length for it to be coagulated, and this is brought about more quickly according as the aspirating pipe facilitates the evaporation of the solvents, which may at the same time be recovered. Before a complete revolution has taken place the coagulated film is borne away upon a separate roller, and from thence upon the drying rollers in a drying chamber, being finally rolled up upon a small drum after complete drying.

The drum surface is composed of a sheet of nickel firmly pressed upon a metallic drum. This sheet for drums of very great diameter is formed of nickel sheets riveted one upon the other on the under side, so that the surface may be perfectly smooth.

THE EMULSION PROCESS.

Before depositing the sensitive layer upon the film this should be coated with a substratum, otherwise the layer will not adhere.

The emulsion process is carried out by spreading an emulsion over the film by a method analogous to the formation of the pellicle itself.

Thornton's process. Fig. 155 represents the apparatus. The spreader is here replaced by a coating roller. A cylinder *B* is destined to bring the emul-

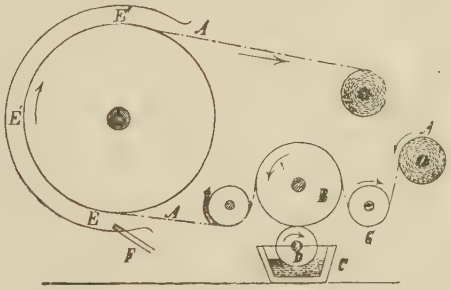


FIG. 155. Thornton's Emulsion Process.

sion upon the film *A* rolled upon a drum. A vat *C* contains the emulsion solution and a cylinder *D* is partially immersed in the vat, being in contact with the drum *B* and turning in the opposite direction. The film passes upon the cylinder *B*, which is coated by *D*, and deposits its emulsion upon the film. The latter is then taken by a roller to a large drum upon which it is partially

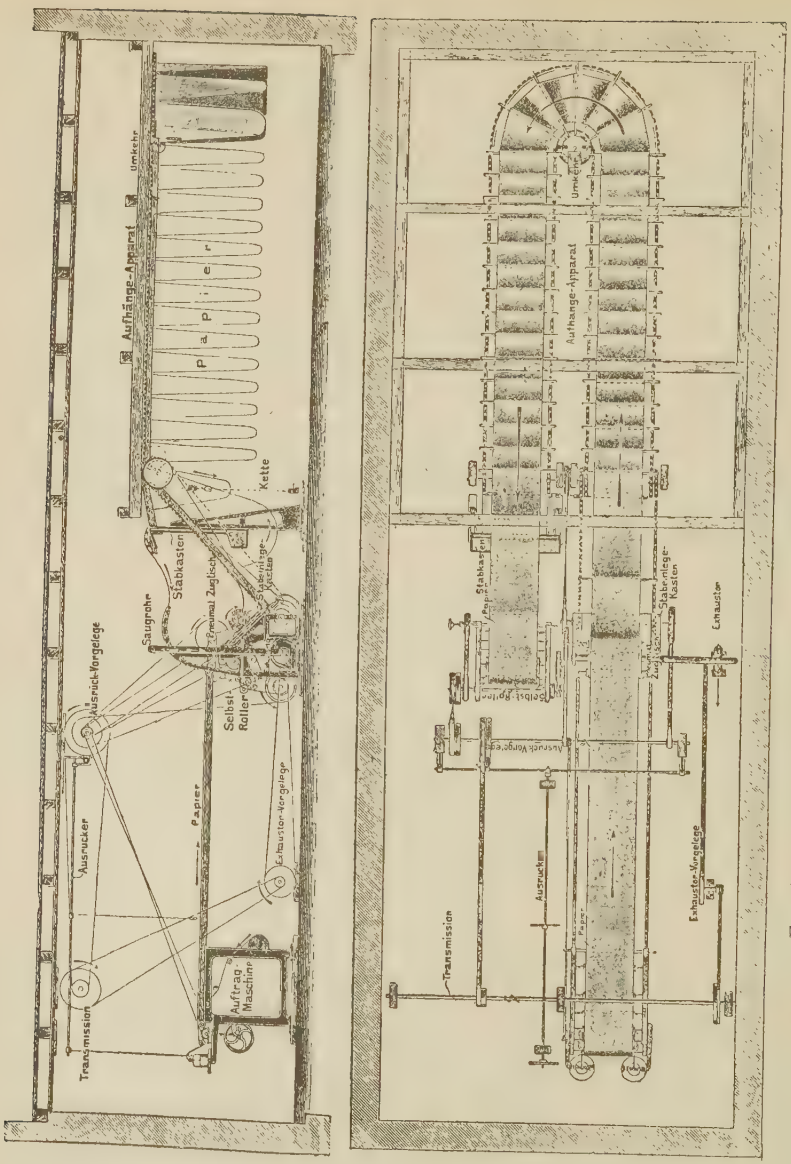
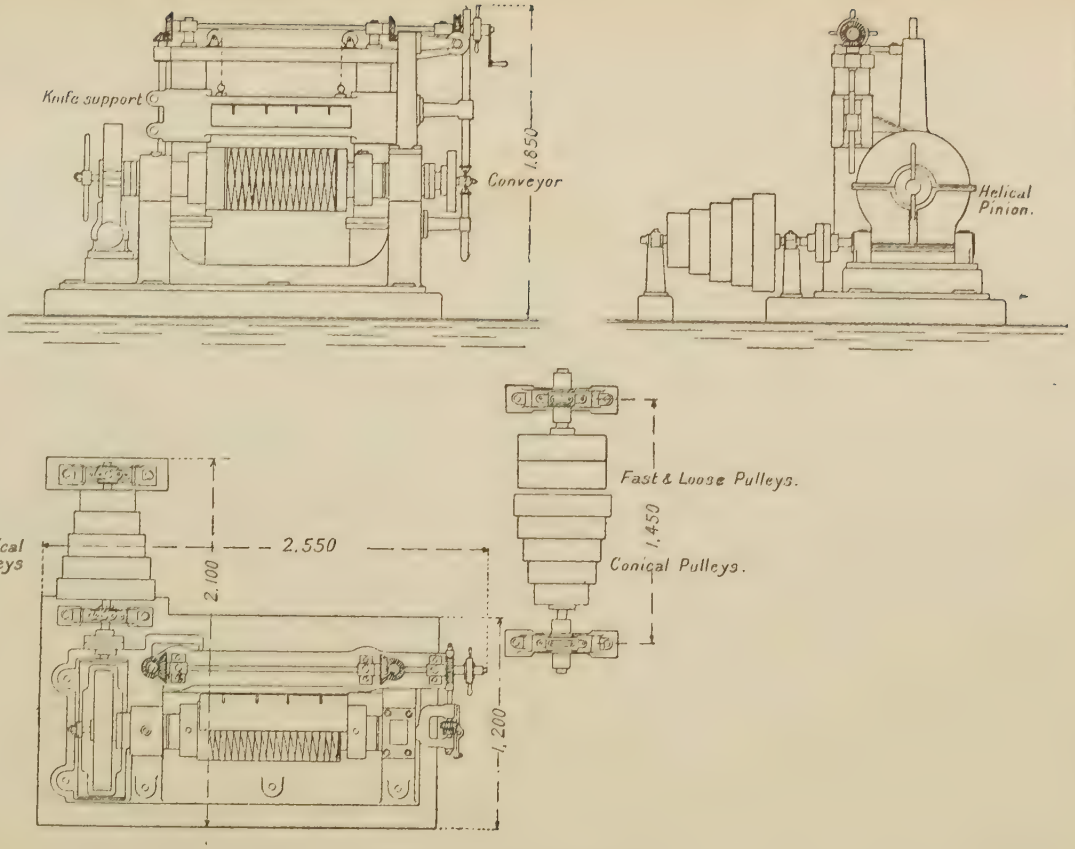


FIG. 156. The Radebeuler Maschinen Fabrik Installation for Emulsions.

Transmission = Power.
Ausrücker = Belt shifter.
Ausrück-Vorgelege = Disengaging gear.
Aufhängeapparat = Hanging apparatus.
Umkehr = Return.
Saugrohr = Aspirating pipe.
Stabkasten = Shaft box.
Pneumat. Zugtisch = Table with pneumatic apparatus.
Auftragmaschine = Coating machine.
Exhaustor-Vorgelege = Aspirating gear.
Selbstroller = Automatic winder.
Exhaustor = Exhauster.
Stabeinlege-Kasten = Shaft entrance box.
Kette = Chain.



FILM CUTTING MACHINE

To face page 303

enrolled. This drum is surrounded by a drying chamber *E*, into which pure dry air is drawn by the pipes *F*. It is then removed and rolled up.

Appliance of the Radebeuler Maschinen Fabrik August Kobig. The wound-up film is developed upon a table, where it is unrolled by a pneumatic apparatus and covered with emulsion, then removed to a drying tube, where it is submitted to the action of an aspirator, and from thence to a hanging arrangement in a drying chamber, where it is suspended as shown in Fig. 156. After drying the film is automatically wound up.

Fig. 156 represents a complete installation scheme.

MANUFACTURE OF FILMS BY CUTTING.

We have seen that celluloid may be produced in cylindrical blocks, with Grether's press, for example (see Part I.), and these blocks cut into sheets by means of a cutter, which produces a spiral cutting during their rotation, thereby giving very thin sheets. These sheets may be employed for the manufacture of films. They present the disadvantage of being deeply striated by the cutting process.

Polishing at this stage presents very great difficulties. The polishing of celluloid in the press is made perfectly by heat and under great pressure, but presses only permit sheets to be polished whose maximum dimensions are 0·65 m. × 1·40 m. It is, therefore, necessary to find another process by which continuous bands may be polished. Calendering will occur to one quite naturally for this purpose.

This process for manufacturing films resolves itself, therefore, into a rolling of the celluloid. But here a difficulty arises, as the rolling is by no means an easy task. In reality celluloid is not a homogeneous substance, but is formed of an intimate mixture of nitrocellulose and camphor, which is far from exhibiting the homogeneity of a metal. On the other hand it is in no degree malleable. In every rolling operation there is an efflux of material, a fact well known to metallurgists. The want of malleability and homogeneity of celluloid does not allow this efflux, or at least only produces it according to the structure of the substance. Again, this process, which should without doubt under certain conditions of pressure and temperature bring about the polishing proper, does not completely efface the very pronounced traces of the cutting machine. The pressure due to the rolling does not, therefore, produce entirely the same effect as the pressure due to the press; it diminishes the thickness much more markedly (ten to twelve times). Upon the films very elongated ellipses may be observed, whose major axes are always situated in the direction of the length.

The polishing in the calender should be made between nickel-coated cylinders One is naturally attached to the pressure and temperature conditions of press polishing, but here, on the contrary, these conditions should be set aside, and a less elevated pressure, or perhaps a series of graded pressures, substituted. If

the polishing is to be by calender, then a calender for satining paper may be employed, of the type Repiquet-Chassagne or Hauboldt, for example (Figs. 157 and 158), but with nickel-coated cylinders.

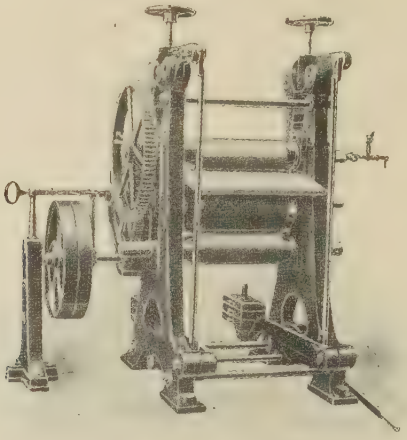


FIG. 157. Repiquet-Chassagne's Polishing Calender.

The results, in spite of some exceptions, have not been satisfactory up to the present. Certain American firms have tried this rolling, only to abandon it for casting.

A new company, faced with this difficulty, has undertaken the polishing of

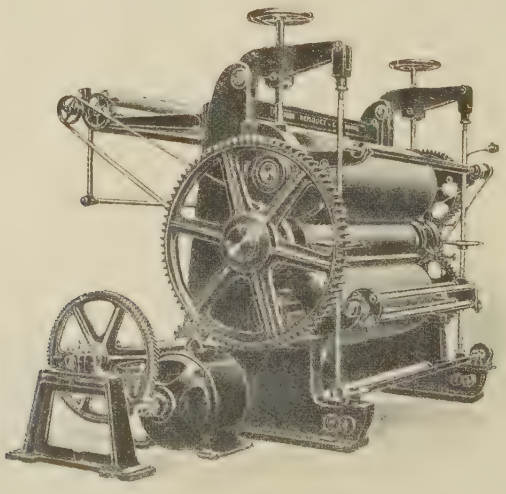


FIG. 158. A Repiquet-Chassagne Polishing Calender.

films in the plate press. This operation appears, however, to present grave drawbacks also.

There remains the process of polishing with acetic acid and pumice. This appears eventually to efface the traces of the cutter.

The interest in this kind of manufacture is such, however, that lack of success has not discouraged research, and almost everywhere the question is being taken up afresh. A new company has even been promoted for this object.

The net cost of manufacture by casting is indeed high, since this process requires very spacious and expensive installations.

In addition, the solvents constitute the greatest danger in the film manufacture and occasion a considerable loss, especially as regards cost. We imagine, therefore, that the rolling of films will retain the attention of manufacturers.

NON-INFLAMMABLE FILMS.

We shall only have a word or two here on non-inflammable films.

The dangers of celluloid most naturally stimulate the research for materials less susceptible of ignition. Formulæ innumerable have been proposed ; very few, however, merit careful attention. These concern films of gelatine, glycerinised or not ; pellicles of viscose ; cellulose acetates.

The former, though of good aspect, are wanting in permanence towards water and are seldom employed.

The second fail totally in photographic baths.

The acetates of cellulose will be dealt with in the third part. They hold actually a very large place in film manufacture, the American acetates being as much in demand as the Cellit of Dr. Eichengrün manufactured by the Farbenfabriken vormals Fr. Bayer.

CHAPTER XI

THE DECORATION OF CELLULOID

Celluloid being much employed for ornaments and fancy articles is the object of a large number of decorating and ornamenting processes, among which polishing, varnishing, staining, gilding and incrustation play the greatest part.

PUMICING AND POLISHING CELLULOID OBJECTS.

Plates, sheets, rods, tubes or celluloid articles may be polished by various methods, such as the disc, French, cylinder, and brush processes.

The disc process. The roller is formed by stamping out felt rings with the punch, a space being allowed in the centre of each for the axle to pass through. At both extremities of this axle an iron disc of about 20 centimetres diameter is placed. Between these two iron discs are placed 40 to 50 rounds of felt, and between them are inserted paper discs. The whole is then tightened by screwing. A roller of this kind, from 35 to 50 centimetres diameter, is driven at the rate of 1500 to 1800 revolutions per minute. The celluloid object is pressed upon this roller. Care should be taken to see that the roller always works against the piece and in the same direction, the pieces being applied to the disc by mounting and pressing. Powdered pumice stone moistened with water is employed as polishing agent, also polishing oil or soap.

The French process. The pumicing roller is formed of a cylinder of soft wood fixed upon a revolving shaft by screws. The cylinder is profiled on its forepart, *i.e.* it presents projections, trenches and flat parts which permit of adjusting objects according as they are concave, convex or plane, into the grooves, projections o flat parts. The roller is covered with leather whose smooth face serves for polishing while the object is pressed to the cylinder. The more exact the adjustment of the object to the cylinder the more perfect the polish.

As pumicing agent a mixture of finely powdered pumice and crude olive oil is used so as to form a paste, or also a mixture of lime tree charcoal in fine powder or tripoli As polishing agent, black soap, rottenstone, or very fine tripoli is used.

The operation is commenced by setting the cylinder in motion, adjusting the object to its profile, and pressing it against the cylinder so that every part may be uniformly well polished. When this result is attained the cylinder is removed and replaced by another of the same profile, but coated with tripoli and oil, and the pumicing continued. The object has then a beautiful polish which is improved by covering it with black soap and applying rottenstone with

the palm of the hand ; then by rubbing with black soap a polish similar to plate glass is obtained.

Cylinder polishing. This process is mainly used for cheap articles. A roller having the greatest diameter practicable is employed, so as to cause objects to have a long path and to augment the rubbing. The objects are placed in the interior of the cylinder which turns about its axis. To obtain a beautiful polish the objects should be left at least 24 hours in the cylinder, in which a polishing agent is placed in the proportion of 10 to 1, fragments of jute, shavings, &c., being also added. The operation is inspected every two hours.

Brush polishing. Upon a shaft revolving at the rate of 3000 turns per minute is fixed either the object to be polished or the polishing brush. For preference a brush of horse-hair about one centimetre long is employed. The brush is fixed in the shaft and contains a polishing agent. The polishing brush is next applied to the objects which are pressed upon it from above. These objects are previously subjected to a rough and rapid polishing by rolling them in a bag with a polishing powder.

THE STAINING OF CELLULOID.

We shall naturally not discuss in this place the imitations of tortoise-shell, mother of pearl, &c., or even products obtained by dyeing the material in the course of manufacture, but will only deal with finished objects which are either stained afterwards or certain portions of them coated with colour.

Celluloid takes up dye very well, being easily penetrated by a solution of dye in alcohol which softens the celluloid. In this way tortoise-shell, ivory, mother of pearl, wood, stoneware, marble, stucco, &c., may be imitated. Various designs may also be painted, while chromo-photography and miniature painting may be carried out. We have seen how a photograph may be transferred to celluloid.

When it is necessary to paint a celluloid object in a single colour, as dolls for example, if the celluloid has not been coloured in course of manufacture, it may be steeped in an alcoholic solution of the dye. The colour may also be applied by brush.

These staining processes do not present anything in particular. Colours not fast to light are naturally avoided.

In order to produce coloured prints on celluloid the ordinary painting and varnishing process may be employed, but good results are rarely obtained, since the colours are not very fast to light and are deficient in transparency. A transfer process may be used as mentioned in the chapter on "Use of Celluloid in Photography." The coloured design made upon chromo-paper is transferred to a collodion film. The film is then withdrawn, after evaporation of the ether from the collodion, and applied upon a celluloid sheet freshly treated with a half per cent. collodion solution. As soon as the solvent has evaporated the print is reproduced on the celluloid, and the collodion may be removed.

As solvent, ether or a chloroform lacquer may be employed.

In order to avoid in the reproduction of large prints by this process the formation of holes and flexures, the print is covered until the hardening of the lacquer by a porous material or kind of canvas which is compressed upon it. The removal of the chromo-paper is made by tepid water.

The colours for staining celluloid should be mordants or their application should be like that of a mordant, *i.e.* of a substance which can penetrate the celluloid more or less deeply according to the porosity of the surface thus staining the mass, or which on account of its chemical nature attacks the surface of the objects, softening or dissolving it, so that the colour itself forms part of the surface of the object. The fastness of these dyes and their brightness varies according to circumstances. The usual celluloid solvents for staining are alcohol acetic ether, acetic acid, acetone, &c. Some dyes may not be employed with these solvents owing to a colour change under their influence, *e.g.* blues. Colours in alcohol act slowly, and a more rapid result is obtained with other mordants. The coloured solutions with these mordants are laid on to obtain a convenient intensity of shade.

The mordants are applied by several methods: immersion of objects in the bath, laying on the mordant, sprinkling. The most rapid process is immersion, but it is difficult to obtain a very uniform layer by this process. On the other hand, if the articles have been previously impressed, one cannot avoid the colour accumulating in the hollows of the impression. In this case it is necessary to retouch with the brush to remove excess. The quantity of mordant should not be too weak in the colour. For perfectly dull shades the mordants are of less importance than for design colours. The dyes dissolved in alcohol, ether, acetone, acetic acid, &c., possess the advantage of being scarcely attacked by ammonia, which is always present in the air, and of resisting the action of the handling, &c. Acetic anhydride, which is sometimes employed as a mordant for making some very fine colours direct upon unprepared celluloid, and without which exposure effects in shop windows are to be feared, forms a chemical combination with celluloid.

Monnier employs the following process: the celluloid is first subjected to the action of softening agents such as acetone, acetic acid, acetic ether, alcohol, methyl alcohol, ethyl acetate, &c., alone or mixed. The dyes, more particularly the aniline colours, are mixed with these solvents and the celluloid dipped into the mixture. The duration of treatment varies from 10 to 20 minutes, and should not exceed the time necessary for obtaining a sufficient softening, which would cause the deterioration of the celluloid if too prolonged. The hardening takes place by drying in air.

The following are the most current staining processes:

Black. The object is dipped in a solution of soda, then in a weak silver nitrate solution. The celluloid is attacked and covered with a sensitive layer, which darkens in sunlight. A black dye soluble in alcohol may also be used and laid upon the celluloid.

Blue. A solution of indigo in sulphuric acid is employed and neutralised by potash. Or Prussian Blue may be deposited by immersion in a bath of ferric chloride, and, after drying, dipping into a bath of potassium ferrocyanide.

Green. The celluloid is dipped in a solution of two parts verdigris to one part ammonium chloride.

Yellow. The object is immersed in a solution of lead nitrate and then into a solution of neutral potassium chromate. Alcoholic solutions of auramine, chrysoidine and aniline colours in general may also be used.

Red. The object is dipped in a very dilute nitric acid solution, then into an ammoniacal solution of carmine.

Purple. The celluloid is dipped in a weak solution of gold chloride and dried in the hot sun.

Brown. A solution of potassium permanganate made alkaline with potassium carbonate is used, or an alcoholic solution of Bismarck brown.

THE VARNISHING OF CELLULOID.

Objects which have been worked, and whose surface lacks lustre, need to be varnished. The varnishing of celluloid is made in a very simple way by brushing upon the object a thin layer of a varnish formed of a solvent or mixture of solvents. The solvent attacks the surface of the celluloid and imparts lustre to it. We have seen that at Oyonnax in the comb industry acetic acid is employed, the operation being known as passage through the acids. (Combs, p. 216.)

Different varnish compositions are employed, all with one or several celluloid solvents. The compositions should attack the celluloid without acting upon the ornaments which may be incrusted upon it, such as gold, silver, jewels, &c.

In general a mixture of solvents is used, *e.g.* acetic acid with a little ether or a mixture of acetone and ether. A little nitrocellulose may also be added to these solvents. The following formula, for example, may be employed:

Nitrocellulose	2 gr.
Camphor	0·1 „
Castor oil	0·1 „
Pure methyl alcohol	50 c.c.
Ethyl ether	50 „

PRINTING UPON CELLULOID.

Printing is a means of decoration frequently employed. This printing, in black or colour by ink, can only be made after a preparation of the celluloid, because the ink is badly absorbed or gives burrs when laid on. The surface must therefore be prepared.

The first operation consists in subjecting the celluloid to the sand-blast machine. For this purpose the machine of Fahdt may be used. The sand-

blast produces a fine compact granulation. The sand-blast possesses the advantage over other processes destined to roughen the celluloid surface of giving a large output, occupying a small space, and capable of easy use. The operator has always under his observation the object undergoing the process.

After undergoing the sand-blast, the celluloid should be washed with water to eliminate the sand particles which have incrusted the surface. It is next submitted to a washing with alcohol, and coated with a varnish formed of two parts linseed oil, one part of white copal varnish, and one part spirits of turpentine or lavender. The varnish penetrates in the celluloid pores formed by the sand-blast. The celluloid plate or sheet may then be coated with a fine powder composed of dry magnesium and barium sulphates in equal parts, and the action prolonged for several hours. The surface is cleaned and strongly pressed. A surface is thus obtained which takes an impression very well on account of the numerous microscopic pores which are produced upon a very thin layer, and are filled with a substance which forms a mixture with the thick elements of the printing ink, retaining this ink as well as paper.

The printing may also be performed by several processes. Fritz Meyer's process, of Bingen on the Rhine, consists in printing upon paper the patterns to be reproduced upon celluloid and transferring them to it. The latter is impregnated with a solvent, *e.g.* alcohol, ether, &c. The paper is then applied under pressure upon the celluloid. The solution partially dissolves both the celluloid surface and the ink from the paper, and, by pressure, it penetrates into the celluloid carrying with it the printing ink which reproduces the design.

Another process consists in covering the celluloid with a layer protecting it against the action of moisture and perspiration, if it is acted on by linen, and friction.

According to Johann Artner's patent it is covered with a varnish composed of:

Copal dried at 100° C.	6·48 per cent.
Alcohol	16·40 „
Water	1·20 „
Ether of density 0·725	75·47 „
Spirits of turpentine	0·45 „

This varnish is prepared by dissolving the dry powdered copal in ether, adding the water and alcohol, then some drops of spirits of turpentine.

The celluloid surface is dissolved by the ether and alcohol, and the varnish then penetrates it. The spirits of turpentine renders this varnish supple, since it must not become brittle. The celluloid is printed by pressure as previously, and immersed in the varnish whose layer prevents the ink from escaping.

It is finally dried between 50° and 57° C.

According to the process of Neupert of Altona the celluloid surface to be printed is coated with a paste of equal parts wax and potash, with the addition of

water and spirits of turpentine. The design to be reproduced is made with colours dissolved in alcohol and placed above; the alcohol and alkalies partially dissolve the wax which is insoluble in alcohol alone and the colours penetrate the celluloid.

The Rheinische Gummi und Celluloïd Fabrik, of Neckarau-Mannheim, replace the alcohol as colour solvent by acetic acid. The celluloid surface is impregnated with spirits of turpentine.

The process of Hofer and Co., of Zurich, permits the direct printing of colours on celluloid. To the lithographic ink is added a mixture composed of:

Ether	15 per cent.
Camphor	30 „
Paraffin	15 „
Oil and solution of manganese in ether	40 „

This mixture is added to the ink in greater or less quantity according to the nature of the impression, which is made according to ordinary lithographic processes.

Finally, a decoration process with Venetian enamel consists in transferring the image from the typographic paper coated with gelatine and collodion, and making the transfer upon celluloid. This is the same process as that reported for the transference of photographic images.

GILDING.

Gilding is done in the press. It is performed either by colour or by gold leaf, analogous to that employed by decorative gilders. White of an egg, diluted with water, is used as an adherent in the proportion of 8 to 10 per cent. The gold leaf is placed upon a metal stereotype, either of copper or steel and perfectly polished, or of gilded iron, which is fixed to the plate of a gilding press heated between 80° and 100° C. The celluloid surface to be gilded is coated by a brush with white of an egg and gold leaf placed above.

For preference the knee press is employed, which also serves for stamping celluloid, and which possesses the advantage of easy and exact adjustment by means of a crank handle situated under the table.

The press is first adjusted and the pressure then applied by lowering the lever.

When the pressing is over, the polishing is made by means of soft felt, and the sheet allowed to rest upon fairly thick paper for some time.

Fig. 159 represents a knee gilding press of the firm Bouchholtz and Co., of Paris.

The printing capacity of this press varies according to the work. By preparing the objects to be gilded upon plates, and removing the gold which is superfluous by special operators, a workman who only works the press can gild, for example, 4000 combs per day.

Heavy gilding may be made by means of ordinary bronze powder. The

operation is performed by a steel stamp which impresses the object. The gilding compo consists of bronze powder mixed with Dammara resin and turpentine. It is applied by means of a brush, and after drying is washed with spirits of turpentine. This process is not convenient for celluloid sheets of a less thickness than 0·5 mm.

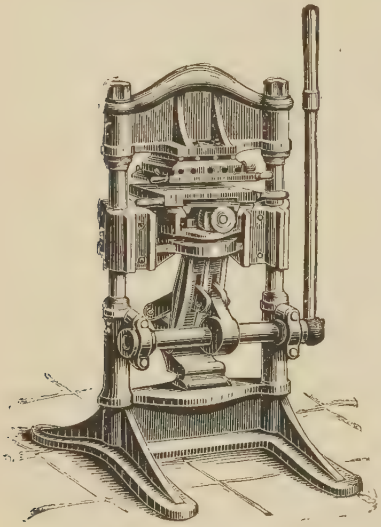


Fig. 159. Knee Gilding Press.

Finally, gilding and silvering may be made by means of a lacquer with which the celluloid is coated according to determined designs, and which is made to penetrate the celluloid by means of a solvent. The parts which should not be decorated are coated with a lacquer layer, and upon the silver layer a coat of gold is laid down by electrolysis and the lacquer layer then dissolved.

INCRUSTATIONS.

Metallic incrustations may be made by introducing metal plates or jewels into the celluloid mass. The operation is thus one of mounting, and the plate is incrusted in the celluloid according to the ordinary incrustation processes by stamping the metal into the hot celluloid in the press.

A recent process patented by La Bellignite consists in introducing the jewels or plates of cut metal into the celluloid when in the pasty condition and allowing to harden.

The incrustation is also made by means of powders. The design is made by means of ink composed of collodion and gold or silver powder, and the sheet placed upon a thick smooth zinc plate which is heated from about 125° to 130° C., and then submitted to a feeble pressure between two cylinders. The pressure causes the design to penetrate into the softened celluloid.

Whatever the process employed the object is polished with very fine pumice powder.

For protection against atmospheric agents the object may be coated with a thin collodion film.

CHAPTER XII

VARIOUS USES OF CELLULOID

We have described the principal uses to which celluloid is put; it is also employed for a large number of other purposes in which the celluloid is subjected to general processes which, however, present nothing out of the ordinary. We shall only mention rapidly the majority of these uses with their mode of manufacture.

Optical uses. Celluloid replaces horn and ivory, and imitates tawny leather for the mountings of lorgnettes, opera glasses, lenses, &c. It is also used for telescope and field-glass frames.

These mountings are cut from sheets. Those destined for glasses are formed of an outlined celluloid sheet, welded and placed upon a cardboard body.

The rims of glasses and sides are cut from a block, or formed of two plates fastened together by solution.

Hairpins. Hairpins are cut from rods of the size desired and pointed at both ends.

The rod may be cut sloping, so as to avoid loss of material.

The Société des Etablissements Petitcollin has patented a different process which permits an economy of material and time, and consists of a drawing operation.

The process is as follows, Fig. 160 representing the machine:

If a length $A\ B$ of a rod stretched horizontally (Fig. 160) be softened, whose extremity A is fixed and the other B subjected to a pull T of known value, it loses its strength and an elongation is produced with diminution in diameter of the elongated part.

In consequence, if a point O on the rod $A\ B$ (Fig. 160) be considered, and if symmetrically to the right and left of this median point the softening of the material is made in a decreasing amount so as to be zero at the points $P\ P$, the elongation and consequently the diminution in diameter proceed in a symmetrical decrease from the point O to the points P, where they are nil. The rod, which was cylindrical from one end to the other, presents after the operation a tapering or gradual thinning out which commences at P and is a maximum at O. Two spindle shapes are thus obtained opposing each other.

Therefore, if upon a rod of any length whatever a certain number of points O dividing the total length into n parts are marked, and if the extremities of this rod are pulled, after having produced a regulated softening about each point O according to the method described above, a rod of greater length will be obtained and constituted of $n - 1$ pointed spindles, welded end to end which only need to be cut.

From a rod of 125 centimetres, 10 pins of 125 millimetres may be made by the older cutting process. With Petitcollin's method, if 16 points *O* distant 83·5 millimetres be heated, and the rod elongated from these 16 points by an amount

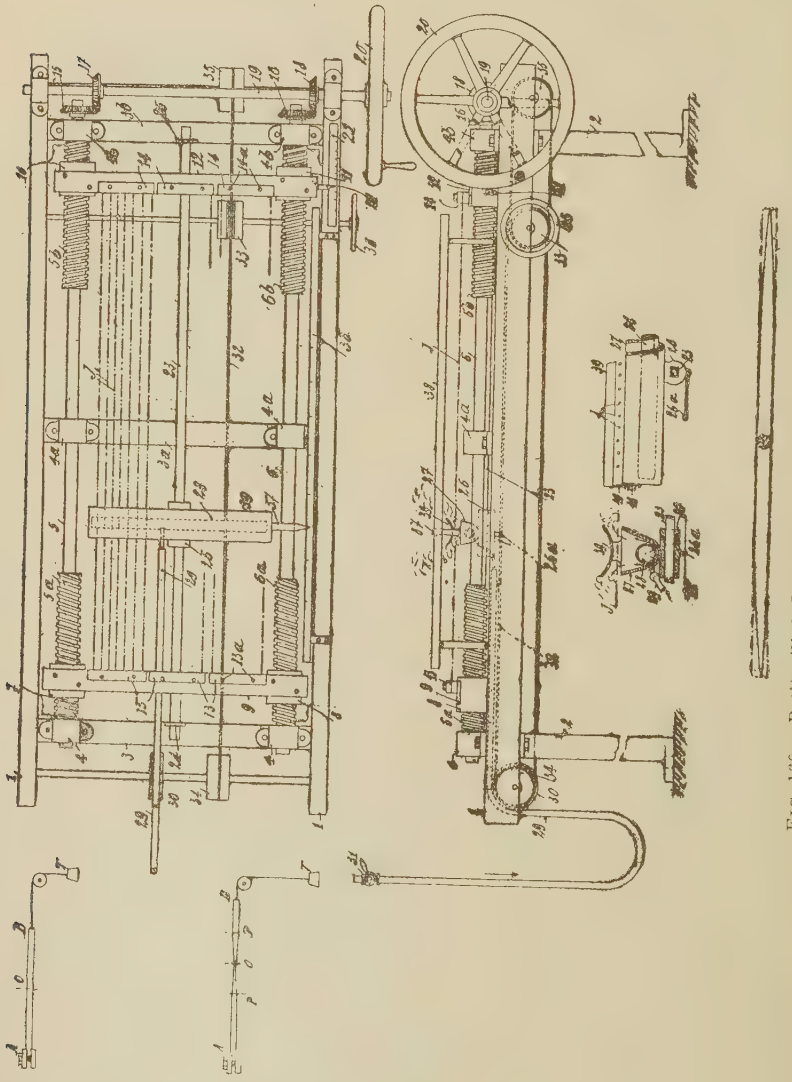


Fig. 160. Petitcollin's Machine for Drawing out Spindles.

sufficient to bring it to 188 centimetres in length, 15 spindles of 125 millimetres are obtained in place of the 10 manufactured by the older process. The economy in material reaches 50 per cent., and this operation dispenses at the same time with the delicate and dangerous operation of pointing the pins.

The machine is arranged as follows:

A frame 1 is joined by a tie-piece with the cross-pieces 3, 3*a*, 3*b*, carrying the bearings 4, 4*a*, 4*b*, in which turn two parallel shafts 5, 6, each terminated at their extremities by screws of contrary pitch 5*a*, 5*b*, 6*a*, 6*b*. The screws 5*a*, 6*a* carry the nuts 10, 11 respectively. Upon these cross-pieces clamps 13, 14 are arranged, in which the rods *J* to be worked up are fixed at their extremities. The shafts 5, 6 each carry a pinion 15, 16 connected with the driving pinions 17, 18, keyed to the shaft 19. By rotation of the fly-wheel 20 the approach or retreat of the cross-pieces 9 and 12 is determined, and a needle 21 fixed to the nut 11 is displaced with regard to a scale 22 carried by the frame for controlling the displacement.

In the horizontal axis of the machine frame a bar or guiding rod 23 is arranged, upon which slides a cylinder 26 carrying a box 27 for steam heating, which extends transversely under the row of rods. A perforated tube 28 arranged along this box receives the steam from a flexible pipe 29, which is rolled over a drum 30 in proportion to the longitudinal displacement of the box. The sliding piece 26 is attached at a point 26*a* to an endless chain or cable 32, which passes round a drum 33. A small hand wheel 36 permits the drum 33 to be moved, and to obtain the displacement of the slider 26 and the box 27. Along a scale 38 fixed to the frame a needle 37 is displaced, permitting the displacement of the box to be controlled. This is surmounted by a cover 39, against the lower face of which rebounds the steam jet, whose longitudinal edges are more or less raised to distribute the heat at a greater or less distance upon the surface of the rods so as to vary the shape of the pins obtained.

The working of the machine is as follows:

By means of the wheel 20 the cross-pieces 9 and 12 are brought to the zero position indicated on the scale 22, so that the arrangement between the clamps 13 and 14 is equal to the dimensions of the unfashioned rods. The rods are clamped and the box 27 brought against the cross-piece 9. The cover 39 is placed on the box 27, and steam sent into the tube 28. The desired heating being obtained, the wheel 20 is turned so that the needle 21 may be opposite the first division of the scale.

This result obtained, the box 27 is rapidly brought by the wheel 36 to the first division of the scale 38, the lid 39 suitably fitted, the operation recommenced, and so on.

When the rods are withdrawn from the machine, they have the appearance of spindles welded end to end, which it suffices to cut and finish. It is well to remark that the rods thus treated may be polished beforehand, thus giving pins with polished points.

Knife handles. Sheets of celluloid are cut by the punch, then stamped and engraved for decoration by incrustation or other processes. The cut plates are next fixed to the blade by small rivets.

The plates may also be produced by rolling between profiled cylinders.

Watch dials. Opaque celluloid is employed, upon which the hour figures are

engraved, or also transparent sheets of celluloid suitably decorated, behind which are fastened paper dials bearing the figures.

According to Kraemer and Elsberg's process both dials are made firm by means of a metal frame, which facilitates mounting and transport.

Frames. Frames may be flat or convex. The former are manufactured by cutting at the press and stamping. Antonini and Grant's process permits frames in relief to be sawn from a single sheet.

Squares, rulers, writing materials. These different articles are manufactured by cutting.

Celluloid of a very pure white variety makes very good drawing instruments when it has been sand polished, and it is utilised for notebooks, field books, &c. Usually writing materials are made from three sheets welded one upon another.

Squares, rulers, &c., are cut according to a stencil by means of a very sharp knife or punch.

Fountain-pen cases. The manufacture consists especially in mounting. The shapes are very varied, and accordingly tubes, handles, &c., have to be worked up by the usual processes.

Pens. Pens are manufactured from thin plates, which are press stamped and finished by chisel.

Scales of thermometers, hydrometers, barometers, &c. For thermometer or other scales, paper may be replaced by sheets of engraved celluloid. These sheets may be introduced into the tube or not. It is well to remark that celluloid scales may not be employed for thermometers registering temperatures from 80 to 100° C.

Use in orthopedy. Celluloid is also much employed in orthopedy, for corsets and apparatus. The apparatus is first modelled upon the body by means of zinc plates and plaster, then this model is covered with celluloid. Such an apparatus is both light and inexpensive.

It will thus be seen that celluloid is of manifold use, and we hope we have given a comprehensive sketch of the manufacture of the innumerable articles for which it is employed.

PART III.
UNINFLAMMABLE CELLULOIDS AND SUBSTITUTES

The processes in use for modifying the composition of celluloid may be classed into two groups: (1) those rendering the celluloid incombustible by adding to the camphor-nitrocellulose one or more substances evolving incombustible gases; (2) those consisting in replacing the camphor, whose price is high, by a less costly substitute.

The desire for obtaining a body possessing all the industrial advantages of celluloid without the defects of inflammability and high price, has given rise to a third group of processes in which both the camphor and nitrocellulose are entirely replaced. The products thus obtained are really celluloid substitutes, and not celluloid as properly understood. Certain of them present sufficient interest for our attention.

CHAPTER I

UNINFLAMMABLE CELLULOIDS

INCOMBUSTIBLE PROCESSES.

The following is the general principle involved in these processes: if to the constituent elements of celluloid, camphor and nitrocellulose, a third body or composition be added which evolves an incombustible gas during the combustion of celluloid, this gas produced by the hot decomposition of the celluloid creates an atmosphere in which the combustion cannot continue, and therefore the product may have an uninflammable character. This is the principle of rendering the composing materials incombustible, by means of which an atmosphere unsuitable for combustion is generated. Rendering non-combustible by simple immersion would give no result for celluloid, since it is indispensable to introduce the body or the composition into the mass. Since the dangers of fire commence during the course of manufacture, this process has the advantage of eliminating them in part.

The efficacy of these processes is debatable, the evolution of an incombustible gas offering a feeble opposition to the combustion of a body as easily inflammable as celluloid. On the other hand, the addition of extraneous materials, mineral salts in particular, scarcely ensures homogeneous products, and these have properties usually very different to those of celluloid.

In every case the choice of mineral salts to be added may be limited. The elimination of unsuitable salts has been the basis of researches carried out in this direction, but it does not seem after the multitude of patented processes that this limitation has been accomplished.

First of all, hydrated salts should be excluded and only absolutely anhydrous salts employed, the former only giving bad results, *e.g.* brittle, friable celluloid incapable of manipulation.

Celluloid is not a proper solution but a colloidal solution, resulting from the gelatinisation of the nitrocellulose which is diffused throughout the mass. The presence of water in the added salt, causes the solution to flocculate and be deposited instead of diffused. The plasticity of the product is then destroyed.

That it will be necessary to eliminate all salts soluble in water is obvious, since if the salt is soluble it will disappear in contact with water. The celluloid will also rapidly lose its polish, and it will be impossible to carry out ordinary manipulations, especially moulding with hot water.

In addition, all bodies should be eliminated which are able to diminish the power of gelatinising under the influence of alcohol. These substances have not yet been established, so that an opportunity exists for investigations in this field.

Each of the products thus obtained cannot be considered as incombustible, and conscientious inventors have reduced their claims by presenting their products as simply "celluloids which are inflammable with difficulty."

Moreover, the majority of substances added are either incorporated with difficulty or modify the properties of the celluloid.

The principal bodies recommended are chlorides, bromides, phosphates, carbonates, boric acid and borates, silicates, acetyl cellulose, fish glue, dextrine, alone or in mixtures.

Processes with chlorides and bromides. Chlorine and bromine are soluble in alcohol. Chlorine may be incorporated in the form of ferric chloride.

The solutions are made in alcohol and ether, one of ferric chloride, the other of celluloid, and the two solutions mixed. A clear liquid of syrupy consistency and yellow colour is obtained. By open evaporation a mass is left resembling tortoise-shell, which is washed and dried.

Care must be exercised to immerse the product obtained in albuminous water after treating it with oxalic acid, which gives it a slight yellow tint. Without this precaution, the surface of the celluloid alters rapidly under the influence of moist air.

Ferric chloride may be replaced by calcium bromide. The product obtained must be immersed in water acidulated with sulphuric acid, which destroys the calcium bromide, otherwise the deliquescence of the latter would give rise to a wetting at the surface.

Bromide of camphor may also be mixed with nitrocellulose, and castor oil added in order to make supple the otherwise brittle product.

Parkin's process. In this process the mixture employed is an alcoholic solution of the chlorides of magnesium, strontium, aluminium and calcium.

One part of one of these salts, or of a mixture, is dissolved in two parts of methyl alcohol and the solution mixed with a solution of celluloid in acetone. The mixture is heated in a boiler until all the volatile constituents have been eliminated. The final residue is composed of a dry granulated material, impregnated with incombustible salts, which should be mixed with ordinary solvents such as acetone and ether in order to be utilised.

Beau's process. This process resembles the preceding. An alcoholic solution of calcium chloride and an acetone solution of celluloid are made, 20 per cent. of the former are mixed with 10 per cent. of the latter, the solvents evaporated and the residue rolled, washed and dried at the ordinary temperature.

Ancelot's process. Magnesium chloride is used, about 50 grammes being dissolved in 150 grammes of alcohol. On the other hand the celluloid solution is made in the proportion of 25 grammes of celluloid in 250 grammes of acetone, and the two solutions mixed in proportions such that a paste is obtained containing 20 grammes of the magnesian liquor for 100 grammes of celluloid solution. This paste is kneaded and dried.

Every process of adding chloride during manufacture has the advantage of

eliminating the chances of fire in the works. This is the principle of the following processes.

Prost and Michey's process. The nitrocellulose is dissolved in alcohol, ether, methylated spirits or acetone, to which a chloride or a chlorhydrate is added in the proportion of 1 to 20 per cent.; for example, a chloride of zinc or iron and a chlorhydrate of ammonia or aluminium.

The mixture of nitrocellulose and liquids is carefully kneaded and then heated in air-tight stoves. The solvent vapours are recovered in a condenser and the plates withdrawn from the vessels are compressed.

The celluloid obtained is neutralised in a bath of sodium or potassium carbonates.

Stocker's process. This process utilises stannous chloride. A mixture of

Nitrocellulose	100 parts
Camphor	400 „
Stannous chloride	70 „

is moistened with 100 parts of alcohol; the mass is allowed to stand for 12 hours and calendered at 60° C.

Germain's process. This process depends on the use of such salts as phosphates, bicarbonates, &c., which evolve incombustible gases. For preference a phosphate or bicarbonate of ammonium or magnesium is employed.

The introduction is made at the moment when the mass is most fluid, but in every case when all the heating operations are at an end. The celluloid is then strongly compressed.

Processes with boric acid. Parkin mixes 4 parts of nitrocellulose with 2 parts of camphor by means of a suitable solvent, such as alcohol, and adds to it 3 parts of pulverised boric acid.

An incombustible paste of the following composition may also be employed:

Magnesium sulphate	40 grammes.
Potassium bromide	40 „
Pulverised boric acid	96 „
Lead acetate	40 „
Ammonium chloride	150 „
Alum	80 „
Potassium binoxalate	80 „

A paste of nitrocellulose is formed which is washed with running water, then with ammoniacal boric acid. The bleached nitrocellulose is then washed with boric acid, compressed, and after the addition of camphor is mixed with the incombustible paste in the proportion of 33 of the latter for 100 of cellulcid. The whole is heated at 150° or 160° C.

Silicate processes. M. Pillon mixes amyl or methyl silicates, or ethyl bisilicate, with nitrocellulose solutions.

Schmerber and Morane's process. MM. Schmerber and Morane prepare an

uninflammable product which is absolutely without danger by neutralising the inflammability with acetylcellulose.

100 kilogrammes of acetylcellulose are dissolved in 50 kilogrammes of methyl alcohol, or acetone, and intimately mixed with a celluloid, formed by mixing 50 kilogrammes of camphor dissolved in 55 kilogrammes of methyl or ethyl alcohol with 100 kilogrammes of nitrocellulose.

Woodward's process. The incombustible composition is formed of liquefied fish glue; additioned by gum arabic, gelatine, and rape seed oil.

The best proportions are as follows:

Celluloid	1 kil.
Liquefied fish glue	1·500
White gum arabic	0·400
White gelatine	0·100
Rape seed oil	0·400

These substances are employed in the state of a syrupy liquid.

The glue is left to swell for 24 hours in a very dry place with good air access. The receiver is heated on the water-bath to 25° C. and the contents stirred until the complete liquefaction of the gum.

The gelatine is then added and stirred until complete solution, so that no lumps may remain. The receiver is then removed from the water-bath and rape seed oil added with renewed stirring.

After being allowed to swell, caused to dissolve, and clarified by passage through a sieve, it is left to cool in the open air for twenty-four hours.

The skin which forms during cooling must be constantly removed, care being exercised to utilise for the celluloid treatment only an absolutely clear and colourless syrup.

The solution of fish glue may be prepared by allowing 200 grammes of glue in 1 litre of cold distilled water to swell for 48 hours.

During the operation 10 grammes of common salt are added.

The celluloid in syrupy condition is poured drop by drop into a glass or porcelain vessel, carefully stirring the mass of fish glue.

The process demands sufficiently prolonged and complicated operations as to increase the net cost.

The following incombustible composition may also be employed:

Pyroxyline	4 parts
Camphor	2 ,,
Copper chloride	2 ,,
Sulphuric acid	2 ,,
Plaster	4 ,,

Process of La Société industrielle de Celluloïd. Dextrine may also be added to celluloid. The celluloid obtained is yellow and brittle.

Processes employing cellulose isomers, such as dextrine, do not usually afford

satisfactory results, the product is granulous and rough, because the dextrine is not assimilable. La Société Industrielle de Celluloïd has modified this process by replacing the dextrine with one of its chemical derivatives obtained by fermentation with the aid of malt, the solution being facilitated by the addition of weak alkalies such as borax. This derivative, completely soluble in the celluloid, preserves its properties of plasticity and transparence.

The malto-dextrine is obtained from commercial dextrine.

A solution of diastase is prepared and mixed in the proportion of 20 grammes malt per kilogramme of dextrine. For the manufacture of celluloid about 5 per cent. borax is added, and the mixture evaporated down. The celluloid is prepared and the malto-dextrine added by rolling.

The proportions are :

Nitrocellulose	60
Camphorated alcohol	60
Neutralised malto-dextrine	18

MAÏSINE.

By this name is designated a product conceived by MM. Allaire and Desvaux, and obtained by utilising, as albuminoids added to the constituent elements of ordinary celluloid, a substance extracted from maize by treatment with the higher alcohols, amyl alcohol for example, and known by the name of maïsine.

To a mixture of nitrocellulose and camphor dissolved in alcohol, the maïsine previously moistened with alcohol is added. The whole is kneaded, then worked up by the ordinary manufacturing processes for celluloid.

The following typical proportions may be employed :

Celluloid	Nitrocellulose	37·500 kilogrammes
	Camphor	12·500 „
	Maïsine	37·500 „

The product is inflammable with difficulty, and is cheaper than ordinary celluloid since appreciable proportions of nitrocellulose and camphor are replaced by maïsine. Industrial practice, however, is far from having confirmed the experimental results claimed for this product.

CHAPTER II

THE REPLACEMENT OF CAMPHOR

The high price of camphor has led to a search for means whereby it may be replaced in celluloid manufacture. This price has undergone variations, due in part to the Japanese monopoly of this substance. The price per kilogramme exceeded eight shillings two years ago.

Also, on account of the very elevated price of this body, it has been attempted not only to substitute another equivalent substance for it in celluloid manufacture but also to obtain camphor by chemical processes, *i.e.* synthetic camphor.

Before dealing with camphor substitutes we shall say a few words on the manufacture of camphor itself.

NATURAL CAMPHOR.

Natural camphor is extracted from the *Laurus camphor* or camphor tree, chiefly in Japan, China, Sumatra and Borneo.

It appears in the form of a colourless, translucent, crystalline mass, readily cut and fairly elastic. It may only be pulverised after being moistened with alcohol, ether, or chloroform. Its density varies between 0·986 and 0·996 above 6° C. Below it is almost equal to that of water. This property distinguishes it from borneol, about which we shall speak later and which has been confused with natural camphor. The density of borneol is higher than that of water.

Camphor melts at 175° C. and boils at 205° C., but it evolves vapour at ordinary temperatures, which renders it dangerous in industrial manipulations. Its solubility in water is very slight, since water only dissolves $\frac{1}{1200}$ of its own volume. It is on the other hand very soluble in alcohol, ether, chloroform, and oils. It burns easily in the air with a smoky flame.

SYNTHETIC CAMPHOR.

Several processes have been recommended for the manufacture of camphor by chemical means. The general principle is the oxidation of the borneols and isoborneols obtained by various processes.

The initial material is rectified spirits of turpentine or pinene.

Camphor is only to be distinguished from turpentine, whose chemical formula is $C_{10}H_{16}$, by the presence of an oxygen atom, its formula, according to Bredt (1893), being $C_{10}H_{16}O$. The question resolves itself therefore into the oxidation of turpentine, but this oxidation has been made the object of a

large number of methods which do not seem at present to have received the sanction of industrial practice.

In principle these processes consist in transforming the pinene, by hydrochloric acid, into pinene hydrochloride containing the chlorhydric ethers of borneol and isoborneol. The manufacture thus comprises three phases :

(1) Transformation of pinene into pinene hydrochloride or chlorhydric ethers of the borneols.

(2) Obtaining the borneols from these ethers.

(3) Oxidation of the borneols.

Dr. Em. Perrot, professor in the High School of Pharmacy at Paris, has thus estimated the economic value of this manufacture in *Le Caoutchouc et la Gutta-Percha* (October 1907): "The preparation of camphor by chemical means necessitates the use of French or American spirits of turpentine, whose commercial price is fairly variable (from ninepence to one shilling and twopence the kilogramme) and whose total production must be strictly limited. The net cost established upon the price of one shilling and twopence the kilogramme should permit camphor to be obtained at four shillings or even less. This chemical or artificial camphor possesses all the chemical properties of the natural product. There is cause for thinking that the manufacture will be improved, and that it will be possible to obtain better yields."

French spirits of turpentine, $C_{10}H_{16}$, is transformed into pinene hydrochloride by the action of a stream of dry gaseous chlorine.

There are thus formed two isomeric chlorhydrates $C_{10}H_{16}Cl$, one crystalline and the other a liquid.

Various processes are employed for transforming this pinene hydrochloride into camphor. By decomposition with sodium stearate it gives a camphene, and by oxidation of this camphene with chromic acid a camphor $C_{10}H_{16}O$ is produced.

The camphene may be obtained by the process of Béhal, Magnier and Tissier, in which the pinene hydrochloride in presence of acetic acid is heated with lead acetate. One takes for example :

Pinene hydrochloride	1·725 gr.
Glacial acetic acid	5·000 „
Lead acetate	3·200 „

The whole is heated at the boiling-point for 24 to 30 hours, and the precipitate decanted and strained. The acetic solution is distilled, neutralised with chalk, and steam distilled giving camphene with a little of the acetates of bornyl and isobornyl.

These acetates moreover give the borneols by saponification, which may on oxidation yield camphor. This is the process in most common use.

According to the process of A. Dubosc and O. Picquet the campholformic ether resulting from the transformation of turpentine chlorhydrates by fusion with a formate or biformate is saponified by water, and transformed into

borneol $C_{10}H_{18}O$ with regeneration of formic acid CO_2H_2 whose presence easily facilitates the transformation into borneol. This borneol is treated with an oxidising agent, chromic acid for preference, and thus transformed into camphor.

The oxidation of the borneols and isoborneols has been made the subject of a large number of patents.

Potassium permanganate has been found to oxidise borneol in dilute aqueous solution. Also the same result may be obtained by an aqueous chlorine solution, although excess of chlorine should be avoided since this would react upon the camphor already formed.

We shall not enter into a more complete study of the various manufacturing processes for synthetic camphor, which would be a departure from the scope of this book, but will refer our readers to the large patent literature on this subject. Moreover, the attempts at industrial manufacture hardly seem to have met with much success up to the present. The Ampère Chemical Co., which manufactured borneol by treating spirits of turpentine with oxalic acid, has allowed its patents to lapse. In France the Société du Camphre, at the Château de Villetaneuse, has not attained much better success in its manufacture. Camphor from pinene usually possesses the drawback of giving a celluloid which becomes turbid and friable.

We shall only speak here of the synthetic or chemical camphor corresponding to the formula $C_{10}H_{16}O$, and not of artificial camphor. The latter, discovered by Kind in 1802, was manufactured by means of hydrochloric acid and turpentine oil and has the appearance of camphor, possessing its odour, but corresponding to the formula $C_{10}H_{17}Cl$; it is thus unsuitable for making celluloid on account of its chlorine content. Synthetic camphor on the contrary is a chemical camphor, only differing from natural camphor in that it does not deviate the plane of polarised light, while natural camphor is dextro- or lævo-rotatory according to production.

The whole question depends on the net cost of synthetic camphor, and all interest has actually been lost in the latter substance owing to the considerable decrease in price of natural camphor. From ten shillings per kilogramme in 1907 it has fallen to two shillings, and there are no reasons for expecting an advance. The Japanese are even of opinion that they might lower this price to one shilling and sixpence and even one shilling and twopence delivered in Europe.

The production of camphor from Formosa and Japan increases considerably and should even be reckoned with the output from the China plantations. M. Haller, membre de l'Institut, expressed the opinion at the Seventh Congress of Applied Chemistry that it will be impossible for synthetic camphor to compete with the natural substance.

Since 1900 the camphor crop has been a state monopoly, and its sale has been leased. Camphor is sold in two brands A or BB; either compressed and purified camphor A, or crudely pressed camphor B.

Camphor B is merely compressed in the hydraulic press to separate the water and oil; it is delivered in cakes of about five kilogrammes (10 kins), wrapped in paraffined paper stamped by the Formosa Government, 10 cakes being

placed in wooden boxes lined with zinc to avoid any loss by evaporation. The camphor A or BB is a camphor compressed, after sublimation, or crystallisation from benzol, into cakes of 500 grammes, each enclosed in a box of tinned sheet iron bearing the Japanese Arms. A zinc covered chest contains 100 boxes.

CAMPHOR SUBSTITUTES.

Natural camphor has been replaced by a large number of substances. The most employed are acetanilide, mannol, celludol, metacelludol, and gelatine, which are utilised in a large number of celluloid works for celluloids of second-rate quality.

Acetanilide. Acetanilide has the formula $C_6H_5NHCOCH_3$; it is the product of the action of glacial acetic acid on aniline; the operation is carried out warm and under pressure. The body obtained after distillation and repeated crystallisations is presented in the form of lustrous plates, melting at 112° C., and commencing to boil at 295° C.

Acetanilide dissolves fairly readily in denatured alcohol which is employed as solvent; at the ordinary temperature, 1000 grammes of acetanilide require for complete solution 6 litres of alcohol, or in other words 1 litre of alcohol dissolves 166·6 grammes in the cold.

It should satisfy certain conditions, viz. be very white and give an almost colourless solution; moreover, this solution should not possess insoluble matters. Unfortunately this product, which well gelatinises the nitrocellulose, has the inconvenience of imparting to the material into which it enters, a coloration, which, if only slight at the commencement of manufacture, may increase towards the end and give, after some time, a yellow celluloid. Moreover, material including acetanilide is softer than that containing only camphor. Finally, this body yields a celluloid having a density a little higher than that of the ordinary material.

What quantity of acetanilide should be incorporated into the material?

If 17 per cent. of acetanilide be incorporated in the pulp, the celluloid obtained cannot be cut; the material is horny and excessively hard. More than 10 kilos of acetanilide per 100 kilogrammes of nitrocellulose should not be allowed, and some works adhere to a charge of 5 per cent.

The following mixture to be employed for 100 kilogrammes of pulp gives good results: alcohol, 60 litres; camphor, 35 kilogrammes; acetanilide, 5 kilogrammes. In short, although the price of acetanilide may be lower than that of camphor (its price is one shilling and twopence per kilogramme), a very good material cannot be made with this substitute.

Mannol. Mannol is a body whose composition corresponds to the formula

which is that of an ethyl acetanilide, and which is delivered by the Chemische Fabriken vormals Weiler Ter-Meer of Uerdingen (Germany). Actually mannol is presented in the form of more or less voluminous crystals having a light rose colour.

This body has a characteristic bitter and disagreeable odour, and burns with a smoky flame; moreover, mannol possesses the same property as camphor of giving gyratory movements when small quantities are thrown on the surface of water. Its melting-point varies from 50 to 52° C.; its boiling-point is 252° Its solubility in denatured alcohol is very great, 70 per cent. may be easily dissolved and even more.

Mannol, which dissolves nitrocellulose as well as camphor, is rarely employed alone; generally it is used in the ratio of 35 or 40 per cent. The following composition may be employed: nitrocellulose, 100 kilogrammes; mannol, 45 kilogrammes; denatured alcohol, 55 litres.

Mixed with camphor, mannol gives with the latter a product whose appearance varies with the proportions. A mixture of 25 parts by weight of mannol and 25 of camphor melted together does not recrystallise after cooling. It appears that the more the mannol content increases, and that of camphor decreases in the mixture, the easier the mass melts and recrystallises on cooling. This fact would appear to demonstrate that in the manufacture of celluloid with this substitute much of the latter should be employed for little camphor. The best results have been obtained with the following composition: pulp, 100 kilogrammes; mannol, 25 kilogrammes; camphor, 5 kilogrammes; denatured alcohol, 62 litres.

In every case, whatever may be the quantity of mannol entering into the celluloid, the latter has the aspect of ordinary celluloid and burns in the same way, giving off a characteristic easily recognisable odour. The chief objection to mannol is that of possessing a softness which cannot be removed. Moreover, it easily becomes brittle and deficient in body; finally, to manipulate it with hot water is much more difficult than with celluloid. A French firm, however, has succeeded in utilising mannol with complete success. The problem appears to be one of drying, but unfortunately we have no precise data in this respect.

In conclusion, we may add that this substance, whose price is high (three shillings to three shillings and fourpence per kilogramme), is chiefly employed in Germany; it may only be used for the manufacture of second-rate materials.

Celludol. This product, of fairly recent origin, also known as celludine, is a trade secret, but it is easy to recognise by analysis. In every case celludol is offered in the form of very white plates, recalling the appearance of acetanilide. The crystals are odourless and have a slightly bitter taste. The melting-point of celluloid varies between 1?0 and 133°, its boiling-point is 307°, and if the heating be continued the molten mass begins to decompose, evolving copious white fumes; on cooling, a yellow liquid remains of bitter odour and plainly ammoniacal. This peculiarity is especially characteristic. Celludol is insoluble in cold water but entirely in boiling water. Its solubility in alcohol

is fairly great, a litre of denatured alcohol dissolving 125 grammes at ordinary temperatures, which corresponds to 12·5 per cent. It dissolves with greater facility in acetone, nearly 45 per cent. in the cold.

Celludol dissolves nitrocellulose less readily than mannol and acetanilide; more than 10 per cent. may scarcely be employed. With this charge the following formula is advantageous: Pulp, 100 kilogrammes; camphor, 35 kilogrammes; celludol, 10 kilogrammes; denatured alcohol, 54 litres. On account of its greater solubility in acetone the latter solvent may be employed, permitting the incorporation of a greater amount of celludol in the material. In the following formula it forms 20 per cent. of the product: Pulp, 100; camphor, 25; celludol, 20; acetone, 40; denatured alcohol, 40. Celludol may hardly be employed without camphor, and in every case not more than 20 per cent. should be taken. In the following formula only celludol enters: Pulp, 100; celludol, 20; denatured alcohol, 60; acetone, 40.

The use of celludol should be limited, since it gives a less rigid material than that with camphor alone. A great objection to celludol is that it gives a celluloid which burns with even greater rapidity than that with camphor.

Metacelludol. This body has the following properties: a lower melting-point than celludol, being in the neighbourhood of 115° C.; the boiling-point cannot be determined because metacelludol decomposes above 375° C. The appearance and general properties are identical with those of celludol; however, its solubility in alcohol and acetone is superior: 20 per cent. in alcohol and 63 per cent. in acetone.

May these various substitutes be used in mixtures? These different substitutes may be mixed and compositions of infinite variation brought about. Mannol may be mixed with acetanilide, mannol with celludol, acetanilide with celludol, &c. Mixtures of these three bodies may also be used. The following formulæ are per hundred parts of nitrocellulose:

Formula A. Camphor, 10; mannol, 20; acetanilide, 10; alcohol, 60.

Formula B. Camphor, 15; mannol, 15; celludol, 10; alcohol, 60.

Formula C. Camphor, 20; mannol, 10; celludol, 5; acetanilide, 5; alcohol, 60.

Formula D. Camphor, 30; acetanilide, 8; celludol, 4; alcohol, 60.

Formula E. Camphor, 35; mannol, 3; celludol, 1; acetanilide, 2; alcohol, 60.

Formula F. Camphor, 35; mannol, 6; acetanilide, 4; alcohol, 60.

Formula G. Camphor, 30; acetanilide, 3; metacelludol, 4; mannol, 5; alcohol, 58.

Many other substances have been recommended and tried, but without satisfactory results. We give below some recent processes, none of which, however, have afforded a good celluloid.

Let us add, however, that the price of camphor causes much interest to be withdrawn from its substitutes, and, as we have previously observed, there are no grounds for thinking that its price will be subjected to a sensible rise.

GELATINE.

Gelatine should only enter into the composition of celluloids of second-rate quality, manufactured most frequently with waste matters which are fairly dear and of very anomalous composition owing to the diversity of production.

It is ordinarily of lower price than the waste matters, and presents the advantage of not being obliged to undergo the operations of washing and filtration necessitated when waste is used. Gelatines of second-rate quality may be bought at 1·50 fr. per kilo.

Gelatine may be incorporated by three processes, which differ in the mode of solution:

(1) Solution of the gelatine in water; (2) solution in acetic acid; (3) solution in glycerine.

Solution in water. The gelatine is left in contact with water at least 24 hours before rolling. The quantity of water necessary is from 14 to 15 per cent. of gelatine. The solution may be accelerated by using warm water at 40–59° C. The incorporation is made when the gelatine is well dissolved.

Solution in acetic acid. Ordinary acetic acid, which dissolves well and whose price is lower than that of the anhydrous acid, is most usually employed.

The gelatine is placed in a vessel with acetic acid in the proportion of 1 of gelatine for 1·5 of acid. It rapidly brings out solution, and the incorporation may immediately be proceeded with.

Solution in glycerine. Glycerine dissolves gelatine very well, about 12 hours being necessary for dissolving 100 parts of commercial gelatine in 20 to 25 grammes of glycerine.

Of all these solvents glycerine possesses the best advantages. Solution in water would be most economical, but the incorporation of the gelatine thus dissolved is very difficult and the material obtained is inferior to that obtained with glycerine, which gives great suppleness to the celluloid manufactured.

The gelatine may be rendered insoluble by means of formol, the quantity of acid being from 8 to 10 grammes per kilogramme of gelatine employed; this formol is usually dissolved in a small quantity of alcohol.

Incorporation. The gelatine and pulp are kneaded in a machine at 60-65° C., without exceeding the latter temperature. The camphorated alcohol is first poured in, then the pulp, gelatine and solvent, which is usually formolated glycerine.

After about an hour's working the mass is homogeneous; it only remains to complete the operation with the roller. In a short period a very good result is obtained.

Certain firms incorporate up to 40 per cent. of gelatine with the celluloid, but 30 per cent. is sufficient to obtain a good result.

The three following formulæ permit of obtaining 100 kilos of dry celluloid:

(1) *First-class material:* pulp, 75 kil.; denatured alcohol, 47 kil.; camphor, 26 kil.; gelatine, 16 kil.; glycerine, 3·2 kil.; formol, 130 gr.

(2) *Second-class material:* pulp, 55 kil.; denatured alcohol, 34 kil.; camphor, 19 kil.; waste, 25 kil.; 10 per cent. camphorated alcohol, 5 kil.; gelatine, 24 kil.; glycerine, 4·8 kil.; formol, 200 gr.

(3) *Third-class material:* waste, 85 kil.; 10 per cent. camphorated alcohol, 17 kil.; gelatine, 30 kil.; glycerine, 6 kil.; formol, 250 gr.

Whatever may be the gelatine content, provided that it does not exceed 30 per cent., the manufactured material is of good quality, very supple, possessing a beautiful natural polish and capable of ready manipulation. It burns a trifle less readily than ordinary celluloid, and leaves a heavy carbonaceous residue; the only objection to be laid against this material is its susceptibility to moisture, which produces a slight warping.

XYLAMILE.

In 1896 the Société de Chromolithie patented a manufacturing process for a substance analogous to celluloid, but less inflammable and known as Xylamile.

To manufacture it nitrocellulose, which has been rendered pasty by adding to it a mixture of equal parts amyl acetate and amyl alcohol, is heated.

The most convenient proportions are 27 parts by weight of the mixture amyl acetate and amyl alcohol for 50 parts nitrocellulose. A paste is thus formed (which we shall designate A) in a roller heated between 50° and 60° C., and the following composition (which we shall designate B) added to it.

This composition is made up of:

B	Glycerine	$6\frac{1}{4}$ parts by weight.
	Ammonium chloride	$1\frac{1}{2}$,, ,, ,,
	Ceresine	4 ,, ,, ,,
	Aluminium sulphate	$1\frac{1}{4}$,, ,, ,,
	Potassium sulphate	$\frac{3}{4}$,, ,, ,,
	Albumen	3 ,, ,, ,,
	An essential oil such as aspic or another according to requirements	$6\frac{1}{2}$,, ,, ,,

Xylamile may also be obtained in the liquid state. Its composition is then as follows:

B	Nitrocellulose paste	50 parts by weight.
	Acetone	29 ,, ,, ,,
	Acetic ether	$11\frac{1}{2}$,, ,, ,,
	Glycerine	$2\frac{1}{2}$,, ,, ,,
	Ammonium chloride	$\frac{1}{2}$,, ,, ,,
	Ceresine	$1\frac{1}{2}$,, ,, ,,
	Aluminium sulphate	$\frac{3}{4}$,, ,, ,,
	Potassium sulphate	$\frac{1}{4}$,, ,, ,,
	Albumen	$1\frac{1}{2}$,, ,, ,,
	Essential oil of aspic	$2\frac{1}{2}$,, ,, ,,

The preparation is as follows :

(1) The acetic ether and acetone are mixed, allowed to stand, and 50 parts of paste A added to it. The whole is stirred until complete solution has taken place.

(2) The following are dissolved separately :

(*a*) The ceresine in 1½ parts oil of aspic.

(*b*) The glycerine with 1 part of the oil remaining.

(*c*) The ammonium chloride, aluminium sulphate, potassium sulphate, and albumen slightly diluted.

Finally, the three solutions are united by stirring, then the whole gently poured into the solution of nitrocellulose in acetone and acetic ether and stirred to an intimate mixture.

PRODUCTS WITH NAPHTHALENE OR COLOPHONY.

The effect of substituting translucent products such as naphthalene and colophony for camphor has been tried.

Each of these products yields unsatisfactory results in the celluloid manufacture. The material obtained with either is generally deficient in plasticity, and possesses a disagreeable odour.

Colophony may be used together with camphor to give plasticity to the mass.

For example, 50 kilogrammes of camphor are dissolved in alcohol to which 50 kilogrammes colophony are added, which also dissolve. The whole is mixed with the nitrocellulose. In all, only half the camphor of ordinary celluloid has been replaced by the resin known as colophony. The mass obtained is far from having the plasticity of ordinary celluloid.

Naphthalene is equally unsuitable.

The Arbez-Carme process. Naphthalene, better than camphor, and even than crystallised phenol, possesses the property of maintaining a certain amount of colophony in the semi-fluid condition. M. Arbez-Carme has conducted a series of experiments in this field and has determined how the mixture colophony-naphthalene is maintained in a perfectly semi-fluid condition.

By this process he has been able to obtain a celluloid possessing the appearance of ordinary celluloid, and which may be fashioned.

It is capable of taking a beautiful polish but has a disagreeable odour.

The net cost is much diminished, and the inflammability reduced in spite of the presence of naphthalene.

The product has been manufactured by adding 5 per cent. camphor to facilitate solution of the nitrocellulose.

The esters of organic acids have been recently tried, and the acetic esters, in particular, hold an important place among the substances destined to replace camphor.

Of all the acetylated compounds tried very few are suitable, and these only preserve very incompletely the plasticity of the nitrocellulose.

The acetic esters, sugars or corresponding alcohols, such as malite for example, only gelatinise the nitrocellulose very imperfectly.

Amyl acetate, phenoxyacetic ester, and other acetylated compounds of this type, have the inconvenience of being very volatile and of exhaling a very pronounced and disagreeable odour.

Claessen's process. M. Claessen, of Berlin, recommends the use of esters produced by the condensation of benzaldehyde with acetoacetic ester, using small quantities of a base for this purpose, *e.g.* pyridine or diethylamine, since these esters, viz., benzylidine diacetoacetic ester and benzylidine acetoacetic ester, have a remarkable gelatinising influence on pyroxylin.

He concludes that these esters are particularly suitable for replacing camphor either entirely or in part in the celluloid manufacture, and prepares a celluloid in the following way: 3·5 kilogrammes of benzylidine diacetylacetic ester and benzylidine acetylacetic ester are dissolved in 10 litres of alcohol, and this solution poured upon 5 kilogrammes of pyroxylin. The mass furnishes immediately after kneading, compression and heating a translucent gelatine which is heated between 60° and 90° C., and which is submitted to a second kneading. As soon as the mass hardens a little it is compressed under strong pressure.

This process presents, according to the inventor, the advantage that the amount of the substances mentioned to be added is less than that of camphor for obtaining the same result. The proportion is about half.

Lederer's process. This process utilises chloral hydrate or alcoholate of chloral.

A mixture of 2 parts chloral hydrate is made with 5 parts of nitrocellulose. This mixture is manipulated in the ordinary way, with the addition of alcohol, and a material obtained presenting the appearance of celluloid.

Alcoholate of chloral may be employed, by intimately mixing 3 parts of cellulose acetate with 2 parts of chloral alcoholate, and then compressing at a moderate heat.

The author extends his process still further, replacing the nitrocellulose by one of its mixtures with the esters of organic acids, or by the organic acid esters of nitrocellulose, or again by mixtures of nitrocellulose and organic acid esters of cellulose.

Process of the Badische Anilin und Soda Fabrik (Ludwigshafen on Rhine). This firm has patented a process similar to that of Claessen previously described, and which consists in taking benzylidine acetate as base or its monochlor substitution products.

Benzylidine acetate is obtained by acting upon benzaldehyde and its monochlor substitution products with acetic anhydride.

Its melting-point is 58° C., that of its monochlor derivative being 82° C.

The operation is as follows: 1·35 parts by weight of benzylidine acetate are mixed with 100 parts of nitrocellulose in alcoholic solution. The product is then treated in the ordinary way.

If the monochlor derivatives are employed the proportions are as follows:

2·30 parts by weight of diacetate of benzylidine monochloride; 100 parts by weight of nitrocellulose in alcoholic solution.

In another process of this firm the camphor is replaced by chloroacetyl derivatives of aniline.

The proportions according to the compounds employed are:

I. { 1·35 parts by weight of methyl trichlor acetanilide;
100 parts by weight of nitrocellulose mixed with alcohol.

II. { 2·20 parts by weight of ethyl tetrachlor acetanilide;
100 parts by weight of nitrocellulose mixed with alcohol.

III. { 3·30 parts by weight of benzyl tetrachlor acetanilide.
100 parts by weight of nitrocellulose mixed with alcohol.

IV. { 4·30 parts by weight of ethyl pentachlor acetanilide;
100 parts by weight of nitrocellulose mixed with alcohol.

One may also employ 30 parts of methyl trichlor benzoylanilide per 100 parts of nitrocellulose mixed with alcohol.

Finally, this firm has also replaced camphor by aromatic orthodiamines derived from amidines.

For example:

30 parts by weight of methanyl toluylene diamine with 70 parts of nitrocellulose mixed with alcohol, or

35 parts by weight of ethylethanyl phenylene diamine trichloride with 65 parts of nitrocellulose mixed with alcohol.

Meister, Lucius and Bruning, of Hœchst à Main, employ aromatic sulphonic acid derivatives.

The process of Goldschmidt and the British Xylonite Co., of London. This process employs the esters of sebacic acid. 100 parts of nitrocellulose are worked up with 40 parts of ethyl sebate in alcoholic solution; or 100 parts of nitrocellulose are worked with 40 parts of the products obtained by the oxidation of castor oil or cocoanut oil with nitric acid, and the esters obtained fixed with methyl alcohol.

Process of the Rheinische Gummi und Celluloïd Fabrik (Neckarau-Mannheim). This firm replaces the camphor by the sugar esters of glucose, lævulose or saccharose.

Zühl und Eisemann's process. MM. Zühl and Eisemann of Berlin use the phenolic esters of carbolic acid.

For example:

(*a*) 35 kilogrammes of diphenyl carbonate with 60 kilogrammes of nitrocellulose.

or (*b*) 30 kilogrammes of dicresyl carbonate with 70 kilogrammes of nitrocellulose.

or (*c*) 35 kilogrammes of dinaphthyl carbonate with 70 kilogrammes of nitrocellulose.

Ortmann's process. The composition is as follows:

1 kilogramme of pyroxylin.
0·065 litres of turpentine.
0·25 litres of acetone.
0·025 litres of ether.

Add 0·5 to 0·75 litres of methyl alcohol, allow to stand about 12 hours and roll the mass.

Process of the Chemische Fabrik vormals Weiler ter Meer. Camphor is replaced by the mono- or polyhalogenated derivatives of the primary aromatic amines; by the acetylated derivatives of the halogenated aromatic amines such as chloracetanilide, and by the formyl, acetyl, benzoyl secondary aromatic amines, *e.g.* methylaniline.

The process of Béthisy, Fouchard and Vignes. This is the process recently employed by the Société du Celluloïd Uninflammable at Bourges.

The plastic mass is a derivative of tetranitrocellulose.

The tetranitrocellulose being ground up with 40 to 45 per cent. water, is formed by the hydraulic press into cakes, which are then pounded into very fine particles and steeped with the following solvent:

Glacial acetic acid	0·800 kgr.
Sulphuric ether of 65°	20·000 „
Acetone	20·000 „
Amyl acetate	15·000 „
Alcohol	15·000 „
Solution of 10 per cent. Unona selanica	8·200 „

These proportions correspond to a steeping of 100 kilogrammes of pounded cakes. This solvent is prepared as follows:

850 grammes of Unona selanica are dissolved in 7·750 kil. of sulphuric ether of 65° for twenty-four hours, the mixture being stirred from time to time and filtered. The ether, acetic acid and acetone are then mixed together, and after being stirred from time to time for about twelve hours is added to the solution of Unona selanica and sulphuric ether prepared separately.

The whole of the amyl acetate is poured into a bath and the pulverised pulp added to it; it is allowed to stand for about six hours and the whole kneaded. The preparation of Unona selanica, sulphuric ether, acetic acid and acetone is then added, the mixture allowed to stand for about six hours and kneaded; finally the whole of the alcohol indicated above is added.

When the rolled paste has attained a convenient degree of consistency, the cylinders of the rolling mill are cooled and the following substance allowed to flow in:

(1)	Boric acid by weight	50 parts.
	Sulphuric ether by weight	10 „
	Alcohol dried to 75 per cent. over lime by weight	100 „
(2)	Ammonium sulphocyanate by weight	40 „

The solution is thus prepared: the ether is poured upon the boric acid in

order to obtain a strong acid from a weak one, then the lime-dried alcohol is added, and the whole allowed to stand for about twenty-four hours, stirring from time to time; it is next filtered (1 kilogramme of this mixture gives about 0·565 kil. of filtered solution).

The lime-dried alcohol gives an ethoxy derivative of the tetranitrocellulose which is tetranitro-oxycellulose. By the addition of ammonium sulphocyanate the acids are neutralised without influencing the quality of the material, quite the reverse.

After the addition of this mixture the rolling is continued until complete and intimate incorporation.

CELLULOSINE.

MM. Cadoret and Degrand have given this name to a product derived from cellulose in the form of cotton, straw, &c.

The cellulose is successively lixiviated with alkalies and oxalo-saccharic acid. This acid is obtained by soaking 2½ kil. of molasses and 2½ kil. of starch with 10 litres of water.

When the mixture has been well established, 6 litres of nitric acid of 36 degrees is added, and the whole heated.

The product obtained is of great purity; it is dried and allowed to stay in a solution of any bisulphate in sulphuric acid. This first liquor is mixed with another composed of:

1 part of any nitrate;
2 parts of nitric acid.

The body is bleached with the double hypochlorite of sodium and magnesium, the liquid oxalo-saccharic acid drawn off is added, the substance dried and incorporated into a product called celluline, which is obtained by decomposing spirits of turpentine in presence of a metal with a current of gaseous hydrochloric acid.

To secure incombustibility, zinc chloride is dissolved in it.

THE USE OF CASEIN.

It was, natural, on account of the analogies which exist between colloidal cellulose solutions such as nitrocelluloses, xanthates, and cellulose acetates on the one hand and the albuminoids on the other, to seek the replacement of camphor by albuminoids and by casein in particular.

The latter proteïd residue, from the coagulation of skimmed milk, is presented in the form of a white powder, insoluble in water, alcohol, and the ordinary cellulose solvents, but soluble in dilute alkaline solutions, ammonia, soda, sodium, carbonate, borax, &c.

Ammonia is one of the best solvents for casein, but one of the principal inconveniences to its use results from the extremely disagreeable odour which

this liquid evolves, rendering manipulation very troublesome. Casein placed in contact with a dilute ammoniacal solution dissolves fairly rapidly, and after a short time the whole mass is gelatinised ; it is not uncommon to find swellings produced, especially if the proportion of ammonia is great.

The proportion of ammonia to be employed per hundred of casein varies from 16 to 22 grammes, which corresponds to 18 to 23 cubic centimetres of ammonia having a density of 93°. Our personal investigations have given the best practical gelatinisation of casein when employing 21 cc. of ammonia per 100 of casein ; the proportion of water to be employed for steeping is also variable, and while the amount must be strictly limited, sufficient should be present to permit of the whole mass being moistened.

For preference 70 cc. of water, distilled as much as possible, should be employed per 100 grammes of casein. There are therefore present: casein, 100 grammes; ammonia at 10 = 930, 21 cc. ; distilled water, 70 grammes. The casein after being steeped and well triturated by means of a spatula, is placed in a closed receiver so as to avoid the volatilisation of the ammonia. At the end of four to five hours the casein is gelatinised.

Caustic soda does not gelatinise the casein so well, especially with the weak solutions which have to be employed. Borax and carbonate of soda are generally preferred to soda.

Borax dissolves casein fairly well, but one of the principal drawbacks to the use of this body is the giving of an opaque material. The best solution to employ for obtaining a good result is that containing 4 to 5 grammes of borax per 100 of distilled water; when this content is carried to 10 per cent. the borax crystallises in the cold.

The following recipe has given us a satisfactory solution: Casein, 100 grammes ; borax, 9 grammes; distilled water, 225 cc. The above are left in contact in a closed vessel to avoid the evaporation of water, which would give a paste too dry. After a normal period of 24 hours the gelatinous paste may be employed.

Sodium carbonate appears to be one of the best solvents for casein. At least 10 grammes of sodium carbonate are necessary to dissolve 1000 grammes of casein, but to accelerate the solution 15 to 18 grammes of carbonate per kilogramme of casein are used for preference. The proportion of water necessary for a good steeping should vary from 800 to 850 cc. per kilogramme of casein.

Certain firms simply employ distilled water for steeping the casein, but in this case the gelatinisation is only possible during rolling, and is only very slowly produced. Sometimes a part of the water is substituted by denatured alcohol or any other nitrocellulose solvent. In every case we should prefer the use of a cold solvent for casein ; a hot solvent gives yellow products. Of all the solvents examined carbonate of soda is that which has given us the best results.

Commercial casein is habitually impure, and gives turbid solutions. According to Lundberg it is rapidly transformed by alkaline solutions into alkaline albuminates, and it is impossible to clarify the solutions by standing, heating,

or filtration. If this casein, mixed with thirteen times its weight of water, contains 2·5 per cent. of NaO on the weight of the dried casein, there is still produced a turbid solution; but if to this solution be progressively added a 5 per cent. solution of caustic soda, some white precipitate separates when the quantity of soda attains 14 per cent., according to the following Table :

Total caustic soda content per weight of dry casein	State of the casein solution	Remarks
Per cent.		
2·5	Tolerably fluid, grey not transparent	
3·5	A little more liquid than the preceding	
4·5	Similar	
5	,,	
6	,,	
7	,,	
8	,,	
9	,,	
10	Thick jelly	Colour whiter, traces of clots.
11	,,	When a sample is heated, it takes the appearance of whey and on standing does not become completely clear; the starch separating.
12	Similar to the jelly, feebly green, very homogeneous, appearance of starch	
13	Fluid jelly	A sample shaken with cold water separates into liquid and precipitates.
14	Solution perfectly clear, separates distinctly from the white precipitate	

The origin of the use of casein is found in the German Patent 111081, taken out by Adolf Spittaler, of Prien (Haute-Bavière), from which the above considerations concerning the solution by soda have been extracted.

THE MIXTURE WITH NITROCELLULOSE AND CAMPHOR.

While the casein is gelatinising, the steeping of the nitrocellulose is carried out exactly as for the manufacture of ordinary celluloid with denatured alcohol and camphor. When the casein and nitrocellulose are sufficiently gelatinised, the rolling takes place. One commences by taking the casein paste and placing it upon a roller heated towards 55° C. The casein starts from the very first to

be reduced to dust, therefore it is necessary to bring it to the roller cylinders as quickly as possible. After a period, varying with the state of gelatinisation and humidity of the casein, the latter adheres to the cylinders, whose rotation is then increased, while the rear cylinder is cooled and the fore cylinder maintained at its previous temperature. After a very variable period of rolling, the casein is completely gelatinised and presents the form of a supple, yellow, soft paste. It is unnecessary to continue rolling, otherwise the paste would become short and brittle. During the rolling of the casein, that of the steeped nitrocellulose is proceeded with in part. When the latter is sufficiently consistent, it is withdrawn from the rolling mill and the delicate operation of incorporation taken in hand, by first placing the nitrocellulose paste upon a roller heated at 60°, then allowing it to turn for a few instants for the paste to adhere well. Taking next the casein paste, it is incorporated with the celluloid after being careful to cut it into fragments as small as possible. The difficulty is to mix the two pastes, which should have an identical degree of humidity, so as to obtain a perfectly homogeneous mixture. During the whole rolling period for the mixture of celluloid and casein, the paste is cut so as to divide it well. When the mixture is judged to be intimate and before the material hardens, it is removed and placed under the press.

What proportion of casein may be incorporated with celluloid? In principle up to 100 per cent. of casein may be added to the nitrocellulose, and this proportion may even be augmented ; to obtain a celluloid, however, having almost the appearance and properties of the ordinary material, 50 per cent. may not be exceeded, and in many cases it is preferable not to exceed 25 per cent. The greater the amuont of casein, and the less the chances of obtaining a good substitute for celluloid.

Here are some compositions of celluloid and casein. The casein employed in these trials was obtained from the French firm of Clefs (Maine-et-Loire).

Trial I. Nitrocellulose, 1000 gr. ; camphor, 450 gr. ; alcohol, 600 cc. ; casein, 500 gr. ; distilled water, 350 gr. ; sodium carbonate, 12 gr.

Trial II. Nitrocellulose, 1000 gr. ; camphor, 450 gr. ; alcohol, 600 cc. ; casein, 250 gr. ; alcohol, 160 cc. ; ammonia, 6 cc.

Trial III. Nitrocellulose, 1000 gr. ; camphor, 400 gr. ; alcohol, 650 cc. ; casein, 250 gr. ; water, 190 gr. ; ammonia, 7 cc.

Trial IV. Nitrocellulose, 1000 gr. ; camphor, 450 gr. ; alcohol, 600 cc. ; casein, 200 gr. ; water, 350 gr. ; borax, 2 gr.

Whatever may be the formula employed, the material after drying is rigid and very brittle, and after some time the casein assumes a yellow colour, giving a very bad effect. This material, with casein, is moreover only brittle according as the surrounding atmosphere is dry. In wet weather this excessive fragility disappears, and the material may be bent without breaking.

Casein may also be dissolved by phenol ; this solution works well, but the material is not transparent, being strongly coloured a translucent brown.

With casein only products of second-rate quality may be made, and these are only employed for objects unlikely to be in danger of breaking.

CHAPTER III

SUBSTITUTES FOR CELLULOID

VISCOSE—CASEIN DERIVATIVES.

By the side of products derived from nitrocellulose and camphor or of nitrocellulose alone, a large number of bodies have been discovered whose compositions are quite different from that of celluloid, but which may, on account of their physical properties, replace it in the majority of its uses. Although these bodies have nothing in common with celluloid, we believe it necessary to mention them on account of their identical uses. All these compositions have indeed been invented as celluloid substitutes, having a lower net cost and being less highly inflammability.

Among the very large number of bodies conceived, those which have attained up to the present most attention on account of their properties are viscose and viscoïd—the former being the older—also the casein derivatives, bakelite and the cellulose acetates.

To speak truly, these products do not yet possess every quality of celluloid, though all are employed industrially. The most recent, the acetates, seem to have a bright future before them.

We shall only study here the above four types of product.

VISCOSE AND VISCOÏD.

Viscose. The viscose prepared by Cross and Bevan is a sulphocarbonate of cellulose. In the fresh condition it forms a resinous mass, dissolving in water to give a very viscous solution which is highly unstable. It decomposes spontaneously, yielding "viscoïd." It is coagulated by heat.

This instability is a great inconvenience. It may be rendered more stable by dissolving it in an alkali instead of in water.

The manufacture consists in preparing an alkali-cellulose, by causing caustic soda to act upon cellulose followed by treatment with carbon disulphide.

For preference cellulose is employed in the form of paper-paste. Cross and Bevan have invented a treatment by which impure cellulose may be used, thus cheapening the cost. The process consists in purifying these celluloses by treating them with hydrochloric or sulphuric acids. The operation may be performed hot by boiling the cellulose with 2 per cent. acid, or by treating the cellulose with dilute acids in a turbine, and drying at 60° or 80° C. Finally, the cellulose at 120° or 140° C. may be digested with about five times its weight of water acidulated with 1 per cent. sulphuric acid or 0·5 per cent. hydrochloric acid, and then washed. It is next taken to the stamp-mill.

The product obtained is a hydrocellulose more attackable by alkalies than cellulose. This hydrocellulose is treated with caustic soda in an apparatus furnished with stirrers to avoid the formation of lumps.

According to Böckmann the mixture proportions in Cross and Bevan's process are as follows :

Paper paste	1 part
Solution of 20 per cent. soda	1·5 „

The process is commenced by pouring $\frac{1}{5}$ of the soda solution upon the nitrocellulose, then the remainder of the soda is added. The stirring lasts 48 hours. The caustic soda should be pure and not contain more than 3 per cent. carbonate, which hinders the action upon cellulose.

The cellulose may also be acted upon with a great excess of soda. According to Böckmann the proportions then are :

Paper paste	1 part
Solution of 20 per cent. soda	10 parts

It is unnecessary in this case to stir.

The alkali-cellulose obtained is then transformed into sulphocarbonate by the action of carbon bisulphide. For that it is drained in the hydro-extractor, carbon bisulphide added, and the mixture stirred in a closed vessel.

The proportions are :

Initial cellulose	1 part
Carbon disulphide	$\frac{1}{2}$ „

The viscose obtained is yellow and viscous. Water is added to form a solution of 9° and 10 per cent., which is filtered. The solution is then decolorised by the action of carbonic acid or dilute acetic acid, or by dilute sulphurous acid.

A more recent process consists in submitting to the simultaneous action of hydro-extraction and washing by a saline solution. There are taken, for example :

100 kilogrammes of viscose, with 10 per cent. cellulose, and 100 litres of water containing 10 per cent. of marine salt, and 10 per cent. sodium bicarbonate. This is then hydro-extracted. The machine being in motion, a fresh solution of 50 per cent. sodium chloride is poured into the pan of the hydro-extractor (Société française de la Viscose).

A detailed description of the manufacture of viscose would be a departure from the scope of this book. We refer the reader to the numerous patents taken out by Cross and Bevan and by the Société Française de la Viscose.

Uses. This society employs viscose as a substitute for celluloid to imitate horn, wood, &c., according to the process described in its French Patent 351089.

The alkali-cellulose is treated with carbon disulphide according to the ordinary method. The product obtained is digested for one or two days in an alkaline solution at the surrounding temperature without attaining solution. The resulting product is then pounded between cylinders in the cold for about half an hour, and allowed to stand for 24 hours.

It is next passed to the stuffing to render the mass homogeneous, and finally

moulded. The moulds are placed in a stove at 30° C. for 24 to 36 hours. A homogeneous mass is thus obtained which may replace celluloid.

Viscoïd may also be employed.

Viscoïd. This is obtained by the spontaneous decomposition of viscose, forming a hard yellow mass presenting the appearance of horn.

This product may replace celluloid in many of its applications. It is especially suitable for replacing horn or ebony, and may be manipulated like celluloid, taking a beautiful polish, although its appearance leaves much to be desired.

Pellicles or films. Pellicles or films may be formed by spreading the viscose upon glass or polished metal at a temperature in the neighbourhood of 80° C. These films are cheaper than those of celluloid, and are transparent and non-inflammable, but deficient in tenacity in the baths.

Finally, viscose is much employed in the manufacture of artificial silk.

SUBSTITUTES DERIVED FROM CASEIN.

We have seen that casein may be substituted for camphor, in whole or in part, in the manufacture of celluloid. Casein has also been employed alone as a celluloid substitute. Many processes have been carried out without great success, however, and we shall only quote some processes, differing especially in the casein solvents employed, reserving a greater space for "galalith," which has found industrial application.

VARIOUS PROCESSES.

Lactite was obtained by Callender, who separated the casein from milk, heated it at about 40° C. with a little pure water, and kneaded with borax dissolved in pure water.

Cornalith is manufactured with purified commercial casein, which is dissolved by neutral sodium sulphite. It is then treated with a sulphite compound of formaldehyde, which renders the material unalterable, and afterwards left to dry for several days.

Lilienthal obtains a plastic mass by compressing casein with the sixth of its weight of a mixture of 3 to 4 parts marble or limestone and 1 part of strontia.

Horn obtains a casein mass by mixing 200 parts by weight of water; 100 parts of casein; 5 to 10 parts of potash; 10 to 20 parts of sulphur. After evaporation the residue is dried.

W. Reetz mixes a solution of casein in acidulated water with formaldehyde.

The Casein Co. of America dissolve casein in an alcoholic solution of an alkaline hydrate, neutralise by an acid and add formaldehyde.

The formolisation is, moreover, a coagulation process much employed at present, notably for the manufacture of galalith and analogous products.

GALALITH.

Galalith is chiefly manufactured in France at Levallois-Perret by the Compagnie Internationale de la Galalithe Hoff et Cie, and at Harbourg by

the Vereinigte Gummiwarren Fabriken. It is the sole product derived from casein which is employed industrially.

This substance is obtained by the compression and formolisation of commercial casein.

The casein is reduced to fine powder and kneaded with water. The paste thus obtained is compressed in the hydraulic press to dry it, and subjected to the action of heat which welds the casein molecules together, giving a homogeneous material.

The product is then treated with formol or formaldehyde.

The Vereinigte Gummiwaren Fabriken, of Harbourg (Vienne), replace the caustic alkalies by alkaline carbonates (Ger. Patent 141309), which give colourless solutions of greater clarity, and dehydrate by heat and pressure so as to obtain a compact state. It is then treated with formol to harden the product. It is very important that the formolisation should only take place after precipitation.

Patent 147994 of the same firm mentions the action of acids, and especially of acetic acid, as giving greater plasticity to the material. The casein mass is then mixed with very dilute acid before passing to the press.

Galalith of all celluloid substitutes is that which has received the largest industrial application. It is employed for the manufacture of combs, knife handles, various objects, and particularly for the replacement of horn, whose property it possesses, even its great hardness.

The following is a comparison of the properties of celluloid and galalith according to the experiments of Dr. Hassack and his assistant, M. A. Südey.

The specific gravities of both products are near each other : 1·317 to 1·35 for galalith ; 1·34 to 1·40 for celluloid ; the deviations from these specific gravities result from the incorporation of extraneous materials for colouring purposes. The hardness of galalith is about 2·5 ; that of celluloid is lower than 2.

Both substances are very good electrical insulators. Plates of celluloid and galalith, 2 millimetres thick, have been subjected to the action of a current of 16,000 volts without the plates allowing the slightest current to pass. The great superiority of galalith over celluloid is in its non-inflammability. Under the influence of a flame galalith carbonises but does not ignite.

On the other hand, it is necessary to add that from the practical standpoint galalith is certainly inferior to celluloid.

From the works standpoint celluloid is easily manipulated. It may readily be cut into thin sheets, blades, bands, &c.

Galalith, on the contrary, has the tendency to crack. Nevertheless, it may be worked at the lathe, saw, grinder and borer. Galalith has not yet been obtained in sheets less than 2 millimetres thick, while celluloid may be obtained in sheets as thin as paper. The same is true as regards obtaining threads, which is an impossibility in the case of galalith. Its elasticity is less than that of celluloid. Celluloid objects when bent easily assume their original shape, while galalith breaks under the influence of a relative feeble flexure.

Finally the action of water upon galalith is also an important point. In cold water, galalith, being a very hygroscopic substance, absorbs at ordinary temperatures about 30 per cent. of its weight of water in 6 days; 33 per cent. in 12 days; it swells and assumes a brittle consistency. Celluloid, on the other hand, although a little hygroscopic, does not increase by 1 per cent. of its weight under the same conditions.

Fats, oil, benzene, ether, and alcohol have no disintegrating action upon galalith, neither have acids, but alkaline solutions provoke a swelling, while they are without influence upon celluloid.

Galalith is usually manufactured in plates of 0·40 m. by 0·40 m. or 0·50 m. by 0·40 m. and of varying thicknesses, 2 mm. at the minimum, or in rods 0·75 m. to 1 metre in length and 5 mm. of minimum diameter. Rough plates or unpolished rods are sold from three shillings and sevenpence to six shillings and fivepence per kilogramme, according to the tint, the latter price applying to amber shades.

The use of this substance has been considerable, but its defects exclude it from certain uses.

LEBREIL AND DESGEORGES PROCESS.

The object of this recently patented process (Fr. Patent 408592) is to give casein the suppleness which is generally wanting. It consists in adding about 2 per cent. acetone without solvent action upon the freshly precipitated and dried casein, and mixing the whole in an autoclave heated above 100° C. for about a quarter of an hour. The mixture is then thrown into water.

BAKELITE.

Bakelite, from the name of its inventor Dr. L. H. Bakeland, is a condensation product of phenol and formaldehyde. (It is one of the principal substitutes of celluloid.)

The condensation products of phenols with formaldehyde have been known since 1872, but Ad. Bayer, their discoverer, did not seek to utilise them industrially. Since then compounds of this kind have been successively produced by Kleeberg, Smith, Luft, Blumer, Tharlow, Fayolle, Speyer, Grognot, Helm, Knoll, and Heutsche, whose patents the reader should consult from the historic standpoint. The object of all these processes is to evolve a plastic material, but only bakelite appears able to replace celluloid in a large number of applications.

Dr. Bakeland obtains it by heating phenol and formaldehyde in presence of a base as condensation agent. What however distinguishes his process from those of his predecessors is that while the latter without exception declare it to be necessary to heat below 100° C. he works at higher temperatures.[1] The condensation agents previously taken were acids or alcohols. He only employs the condensing agent in small quantity for obtaining satisfactory results. It seems, moreover, that these bases only work as catalysers.

[1] Communication made to the American Chemical Society, New York February 5, 1909.

According to the author the re-action takes place in three phases to which correspond three products;

(1) *Initial condensation product*, liquid or viscous at ordinary temperatures, soluble in alcohols, acetone, and glycerine;

(2) *Intermediate condensation product*, solid at the ordinary temperature, insoluble but swelling in acetone, phenol and turpentine, and softened by heat.

(3) *Final condensation product*, infusible, insoluble in all solvents, indifferent to the majority of chemical agents, destroyed by heating with concentrated sulphuric acid. Permanent at temperatures near 300 degrees, does not ignite and is a bad conductor of heat and electricity.

By elevation of temperature we pass from one to another of these products, and it is their preparation which constitutes the bakelite process.

Having prepared the first product by the action of formaldehyde upon a phenol, it is heated to a higher temperature than 100° C., dissociation being avoided by maintaining the pressure at 4 to 7 kilogrammes per square centimetre. The heating is conducted in a "Bakeliser" constituted of an inner chamber into which air may be pumped. The temperature is maintained at 160° by a steam jacket and worm.

The bakelite obtained is insoluble and infusible, unattacked by chemical agents, an insulator against heat and electricity, hard, transparent and lustrous. Its density is 1·26. Its resistance to heat, non-inflammability, and cheapness give it a certain superiority over celluloid, but it is inferior to it from the standpoint of elasticity and suppleness.

Bakelite may replace celluloid in many of its uses, viz. for imitation ivory, horn, and amber for stick, umbrella and knife handles, and for phonographic cylinders. A varnish may be made of it which gives great permanence to objects. It is valuable in electricity, dynamo armatures and drums being manufactured of it.

CHAPTER IV

THE ACETATES OF CELLULOSE

CELLULOSE ESTERS.

The numerous compositions designed for replacing celluloid have only afforded very imperfect products. Those derived from paste, gum, &c., are not homogeneous; the albumens, caseins and gelatines are too hard and insufficiently transparent.

It is logical, therefore, that the first researches should be made to test the esters of cellulose other than nitrocellulose.

These esters are non-inflammable, permanent towards moisture, and support alkaline treatment well. The great objection taken to them is their lack of stability.

The esters of cellulose have been made, since the labours of Berthelot and Schutzenberger, the object of a very large number of researches, particularly the last few years. We shall not enter into all the details but reserve a special place for those acetates which actually tend to replace celluloid in certain of its uses, and which moreover appear to have a great future before them.

The following literature may be profitably consulted for the study of the cellulose esters: "Les Ethers de la Cellulose et leurs applications," C. Rivière et L. Clément (*Le Caoutchouc et la Gutta-Percha*, 1909-1910); "Acetates de Cellulose," L. Grognot (*Le Caoutchouc et la Gutta-Percha*, 1907); "La Cellite" (*Idem*, 1908); "Developpements recents dans la chimie de la Cellulose," W. H. Walker (*Journal of the Franklin Institute*, 1907); "Les Acétates de Cellulose," H. Ost (*Zeitschrift für Angewandt Chemie*, XIX); "Le Tetracetate de Cross et Bevan," H. Ost et O. Voigt (*Idem*, XIX); and the numerous patents taken out for several years in this field.

The following cellulose esters have been produced up to date; formates, acetates, butyrates, palmitates, stearates, benzoates and the mixed esters; aceto-nitrates, aceto-benzoates. The acetates are the only interesting ones from the standpoint we now occupy; nevertheless, the other esters have not had the last word said for them, since researches are at present being very thoroughly made with the object of replacing the acetates by other esters which take colour more easily.

The esters are obtained by the etherification of cellulose or hydrocellulose.

The esterification agents are: sulphuric, dimethyl sulphuric, sulphacetic, ortho-, pyro- and metaphosphoric acids, phosphorous oxychloride, di- and trichloracetic acids, sulphonic acids, iodine and chlorine. These agents hydrolyse the celluloid and permit acetylation at low temperatures by absorbing the water of reaction.

As diluent for avoiding a temperature higher than 70° C. during esterification, a neutral solvent of the cellulose ester is employed. This agent is usually glacial acetic acid, sometimes also nitrobenzene, epichlorhydrin and dichlorhydrin. The nitrobenzene must be added slowly, otherwise the reaction instantly ceases.

To obtain the esters solid and stable, they are precipitated by an agent which nullifies the solvent action of the fatty acids, and permits the recovery of these acids or anhydrides.

Usually benzene, petroleum ether (Badische Anilin und Soda Fabrik, Fr. Patent 347906), or carbon tetrachloride (Farbenfabriken vorm. Fr. Bayer und Co., Fr. Patent 371356) are employed.

We shall summarise the chief processes for manufacturing esters other than acetates.

ESTERS DERIVED FROM UNHYDROLYSED CELLULOSE.

Formates. Formic acid is made to act in the presence of sulphuric or hydrochloric acids. The proportions may be from 2 to 4 parts of gaseous HCl, for example, 100 parts of 98 per cent. formic acid, and 20 to 30 parts cellulose.

The Nitritfabrik Aktiengesellschaft has also recently patented a manufacturing process for formates (Fr. Patent 405293).

Butyrates. Henkel Donnersmark's process (Ger. Patent 112817) employs magnesium butyrate. 162 parts of cellulose are mixed with 198 parts of butyrate, dried, and the following added :

Butyryl chloride	213 parts.
Butyric anhydride	25 „

The temperature is lowered by addition of nitrobenzene.

Palmitates, stearates. The reaction temperature should never exceed 90° to 100° C.

The palmitate is prepared by adding 16·2 parts of cellulose to 53 of fused magnesium palmitate ; they are mixed and allowed to dry below 80° C. The product is mixed with 10 parts acetic anhydride and 48 of palmityl chloride. The temperature is lowered by nitrobenzene and the viscous mass precipitated by alcohol.

These various esters have not received industrial application.

ESTERS DERIVED FROM HYDROCELLULOSE.

Hydrocellulose. We distinguish hydrocellulose proper, resulting from the action of dilute sulphuric or hydrochloric acids upon cellulose, and the amyloid resulting from the action of concentrated acids or of zinc chloride in concentrated solution.

Aimé Girard prepares hydrocellulose by immersing purified cellulose in a 3 per cent. solution of sulphuric acid, and drying it between sheets of blotting

paper. After drying and heating for three hours at 30° C. a white, brittle mass is obtained. According to H. Ost (*Zeitschrift für Angewandte Chemie*, XIX) it is preferable to treat with glacial acetic acid to which has been added from 2 to 5 per cent sulphuric acid.

Mork immerses the cotton in glacial acetic acid containing benzene sulphonic acid. Sthamer treats with glacial acetic acid containing chlorine. Cross and Bevan regenerate the cellulose from viscose solutions. They attribute the formula $(C_6H_{10}O_5)_4H_2O$ to the product obtained, and distinguish it from the hydrocellulose resulting from the action of acids on cellulose. H. Ost (*Zeitschrift für Angewandte Chemie*, XIX) contests this differentiation.

Esters of Hydrocellulose. The acetates only are manufactured from hydrocellulose as a starting-point.

CELLULOSE ACETATES.

The acetates are by far the most important esters of cellulose. They have been studied in the first instance by Berthelot and Schutzenberger (*Comptes-rendus de l'Academie des Sciences*, 1869). Their industrial preparation is due to Cross and Bevan.

There seems to be a perfect analogy between the acetic and nitric esters of cellulose. Nitration like acetylation is preceded by hydrolysis. H. Ost and O. Voigt (*Zeitschrift für Angewandte Chemie*, XIX) remark that in both cases there cannot be more than 3 atoms of hydrogen for each group of 6 carbon atoms replaceable by acid radicles. The most strongly nitrated nitrocellulose always contains a little less nitrogen than the formula indicates (see Chapter I., Part I.). This fact is explained in that, not cellulose, but hydrocellulose is nitrated.

From the industrial standpoint this analogy has permitted the utilisation of acetates for certain uses reserved to celluloid, *e.g.* films, leather, papers, and impermeable tissues.

The acetates of cellulose have the great advantage of neither being inflammable, nor even easily combustible. They are soluble in chloroform epichlorhydrin, benzoic ether, glacial acetic acid, nitrobenzene, and a few in acetone and acetic ether.

They have great insulating power, and in consequence are capable of electrical application. Their softness is a defect which has not permitted them for a long time to be used for other applications than films, artificial silk or varnishes. Recently, however, very tough acetics have been obtained, and we have seen objects, such as combs, manufactured with these acetates. It appears, therefore, that a great future may be in store for them.

A solitary objection remains, viz. the acetates cannot be stained.

The first acetate manufactured by Cross and Bevan was considered by them to be a tetracetate. A number of authors have since shown that it should rather be regarded as a triacetate. H. Ost, in particular, repeating a process

given by Perkin for the analysis of acetylated phenols, made the sulphuric saponification of acetyl cellulose. The ester was heated for about twenty-four hours with 50 per cent. sulphuric acid; acetic acid was set at liberty, steam distilled and the distillate titrated. The analytical data corresponded to the triacetate. H. Ost and O. Voigt compare it with the acetate of Lederer and Bayer. W. H. Walker (*Journal of the Franklin Institute*, 1907) admits that there might be present a mixture of di- and tetracetates in proportions such that the index of saponification may be exactly that of the triacetate; he inclines, however, rather to a triacetate.

The triacetate is generated in every formation reaction. It is soluble in chloroform, ethane tetrachloride, nitrobenzene, epichlorhydrin and dichlorhydrin, hot ethyl alcohol and acetic acid; and insoluble in carbon tetrachloride, benzene, petroleum ether, acetic ether, amylacetic ester and acetone.

The diacetate is only soluble in chloroform. It is produced at the beginning of acetylation.

MANUFACTURE OF THE CELLULOSE ACETATES.

Recipes for obtaining acetates are abundant, and a multitude of patents have been taken out during the last few years concerning this manufacture.

The acetates may be obtained starting out from cellulose or hydrocellulose. The hydrolysis should not be too vigorous, otherwise a valueless friable product is then obtained.

Cross and Bevan's process. This is the first in date of industrial acetylation processes. It consists in causing acetyl chloride to act upon hydrocellulose proceeding from the regeneration of either sulpho-carbonate, xanthate of cellulose or viscose in the presence of zinc or magnesium acetate.

The hydrocellulose is mixed with a concentration solution of magnesium acetate in the proportion of 1 molecule of cellulose for 2 of acetate. After drying at 110° acetyl chloride is added progressively in the proportion of 2 molecules chloride for 1 of magnesium acetate employed. It is cooled and stirred constantly, so that the temperature does not exceed 30° C., then washed, dried, filtered and evaporated.

Sthamer's process. 350 parts of acetyl chloride are made to act upon 100 parts of hydrocellulose in presence of 350 parts of glacial acetic acid. (Fr. Patent 340506 and 309759.)

As soon as the reaction slackens concentrated sulphuric acid is gradually added, and the whole heated at 60°–70° C. It is then precipitated by water, compressed and washed with water.

Lederer's process. A mixture of 125 parts hydrocellulose, 500 acetic anhydride, and 25 of 66° B. sulphuric acid is heated between 60° and 70° C. After cooling to about 15°, and the hydrocellulose being dissolved, the ester is precipitated by water.

Landsberg's process. 3 to 4 parts of acetic anhydride containing 1 per cent.

of anhydrous ortho-, meta-, or pyrophosphoric acid are caused to act upon 1 part of Aimé Girard's hydrocellulose. The best temperature is from 45–60°. (Fr. Patent 316500.)

Henkel Donnesmark's process. 1·8 kil. of acetyl chloride plus 1 kil. of acetic anhydride is allowed to act upon 3 kilogrammes of a mixture of equal parts hydrocellulose regenerated from viscose and magnesium acetate.

Processes of the Farben Fabriken vorm. Fr. Bayer.—The starting-point may be either cellulose or hydrocellulose. In the former case (Amer. Patent Miles and Pierce) the proportions are: 200 parts of cellulose, 800 of acetic anhydride, and 20 of sulphuric acid. It is diluted with an equal volume of glacial acetic acid and precipitated by water. In the second case (Ger. Patent 139669) the proportions are as follows:

125 grammes hydrocellulose;
500 „ glacial acetic acid;
500 „ acetic anhydride;
25 „ sulphuric acid of 66° B.

Process of the Société Flora (Fr. Patent 345764). 30 parts of cotton, 70 parts of acetic anhydride (or magnesium acetate), 120 parts of glacial acetic acid, and 3 parts dimethyl sulphate are heated together on the water-bath. After complete solution it is filtered and poured into water.

Corti causes a hot mixture of 120 parts acetic acid and 70 parts of acetic anhydride to act upon cellulose in presence of dimethyl sulphuric acid.

Franchimont's process. By the action of acetic anhydride on cellulose in presence of zinc chloride a triacetate is obtained.

The *Aktiengesellschaft für Anilin Fabrication* (Fr. Patent 368738) replaces zinc chloride by chloracetic acid.

The *Société Anonyme d'Explosifs et de Produits Chimiques* (Fr. Patent 385179) employs zinc chloride dissolved in glacial acetic acid. The mixture is made in the proportion of 2 to 5 of chloride per 100 of the mixture of acetic anhydride and glacial acetic acid, and the operation conducted between 65° and 70° C.

A second process of this firm (Fr. Patent 385180) replaces zinc chloride by sulphacetic acid, and carries out the reaction at a temperature below 100° C.

The processes of W. H. Walker, A. D. Little, and H. S. Work (Fr. Patent 324862). These processes utilise the action of acetic anhydride on cellulose in presence of one of the sulphonic acids such as phenol-sulphonic or naphthol-sulphonic, which gives a regular reaction and a uniform product. By addition of sodium chloride the formation of free sulphuric is avoided, and dilution is made with glacial acetic acid.

The process of Knoll and Co. Acetic anhydride is made to act on cellulose in presence of sulphuric acid (Ger. Patents 180666 and 180667). 1 kil. of cotton wool is treated with a mixture of 5 kilogrammes acetic anhydride, 4 kil. of glacial acetic acid and 0·100 kil. of benzene sulphuric acid. It is left at 40° for 24 hours and a clear viscous solution obtained.

Wohl's process. This process utilises pyridine (Ger. Patent 139669). To a mixture of 10 parts paper paste, 20 parts pyridine and 60 nitrobenzene, 20 parts of acetyl chloride are slowly added. After 2 hours' digestion at 80–90° the acetate is precipitated by an excess of alcohol.

An iodine process. The cellulose is dissolved in acetic anhydride in presence of iodine at a temperature of 120–130°.

MIXED ACETATES.

Acetylbutyrate. This is obtained by mixing 162 parts of cellulose, 168 of magnesium butyrate, 141 of acetyl chloride, and 25 of acetic anhydride, then heating moderately. A product soluble in acetone is the result.

Acetonitrate. Lederer (Ger. Patent 179947) prepares an acetonitrocellulose by the action of acetyl chloride and acetic anhydride upon cellulose at a temperature below 60°.

Such are the principal processes, utilised or recommended, for the manufacture of cellulose acetates. To speak truly, few have yielded good products. Up to recently the acetates have only been manufactured in America and Germany, chiefly by the Farben Fabriken vorm. Bayer und Co., which has put forward the famous Cellit of Dr. Eichengrün, and furnished the bulk of the acetates utilised in France.

Quite recently, however, French firms have investigated some manufacturing processes, and the Société Industrielle du Celluloïd at Paris has just discovered a process giving excellent acetates.

In addition, we know of a manufacturing process also yielding good products which has just been invented by MM. Rivière and Clément of the Société des Etablissements Pathé frères. Other French firms are also investigating this manufacture, and some have arrived at products, which, if they do not give entire satisfaction, are probably not far removed from so doing, and the French industry will very shortly cease to be tributary in this respect to America and Germany.

CELLIT.

Cellit was one of the first acetates to find industrial application.

Discovered by Dr. Eichehgrün, with the aid of two collaborators, Drs. Becker and Guntrun, and after seven years of research, it is now manufactured by the Farben Fabriken vorm. Fr. Bayer und Co., of Elberfeld.

Cellit is a cellulose acetate distinguished from the preceding acetates by the property of giving with camphor a plastic material, when up to that time only brittle substances had been obtained. In addition the previous acetycelluloses were only soluble in chloroform, ethane tetrachloride and nitro-ethane, while cellit is soluble in the much less expensive mixture of alcohol and acetic ether.

It solves therefore the difficulties proceeding from fragility and inherent solution defects of the other acetates, and may be employed for the manufacture of films.

Its great characteristic is its non-inflammability, a most valuable property for a large number of uses. This non-inflammability has been proved by the following experiment:

A celluloid film was exposed to the action of rays from an arc lamp. At the end of three seconds the film ignited. A cellit film of the same kind was exposed to the rays from the same lamp for 10 minutes without any modification in its constitution being detected. When placed in contact with a flame cellit melts, and neither inflames nor begins to ignite.

This substance is plastic, soft and may be cut into strips like celluloid. It is softer than the latter, and this is one of the objections laid against cellit in common with the majority of acetates. Moreover, it is unsuitable for the manufacture of celluloid objects such as combs, boxes, &c., but suitable for the manufacture of films, thin sheets for book-binding, perfume boxes, &c. Beautiful leather papers have been made of it which can be figured and decorated like those of celluloid. It has a good transparence and takes a beautiful polish.

From the standpoint of its use for films, it joins to the valuable quality of non-inflammability a very great tensile strength. M. Paul Liesegang of Dusseldorf has been able to pass a film, 100 metres long, 158 times through a cinematograph apparatus without rupture. A rent was produced at the right side by sticking, which was able to be repaired and the experiment resumed.

The first products offered great inconveniences. The impressions at the end of a certain time wore out, and the films became useless. Since then the manufacture has been improved and this defect has disappeared. One of the greatest difficulties has been to make the emulsion adhere to the film.

The latter problem has been solved by a coating process.

ACETATE OF THE SOCIETE INDUSTRIELLE DE CELLULOID.

This acetate, which we only mention on account of its quite recent appearance, has been discovered by M. Marx, managing director of the company.

From it very beautiful, perfectly non-inflammable combs have been manufactured, and it may be applied for other purposes.

THE USE OF ACETATES.

The acetates were primarily destined for all the uses for which celluloid is suitable, with the advantage of non-inflammability. This, however, has far from been accomplished. Their softness does not permit of their being employed for objects demanding a certain hardness. The addition of camphor permits their usefulness being extended, but a brittle product is obtained.

They cannot be stained, having little affinity for colouring-matters, and it is necessary to incorporate these materials in the mass or have recourse to mordants. This is one of their greatest defects.

[illegible] has been almost restricted to the manufacture

of cinematograph films, covers and leather papers; for rendering tissues impermeable, and for the manufacture of solutions making cotton threads lustrous (Lederer).

As electrical insulators they are very valuable; gold-beater's skins of acetates are very beautiful.

Acetyl cellulose films of the Kodak Company. This company, which produces very beautiful acetates, has quite recently patented a process destined to retard the evaporation of the solvent in the film manufacture (Fr. Patent 408396); this we shall discuss, although its proper place is in the chapter on films.

The process consists in retarding the evaporation of the solvent when forming the sheet by adding a retarding material which will not attack the acetyl cellulose.

Such a substance should have the following properties; it should not affect the sensitive layer, possess a boiling-point relatively much higher than that of the solvent, not give with it any chemical reaction, not alter the transparency, not react with ordinary metals and not be inflammable.

Pentachlorethane, a chlorinated derivative of ethane, having the formula C_2HCl_5 and a boiling-point of 150° C., responds to these desiderata. It is added to the solvent in the proportion of 50 to 100 per cent. on the weight of the cellulose.

As a conclusion to this limited notice of the celluloid substitutes, it must be admitted that few of them have a real industrial value, and that none are able to replace celluloid in all its applications. The best future appears reserved for the acetates.

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